

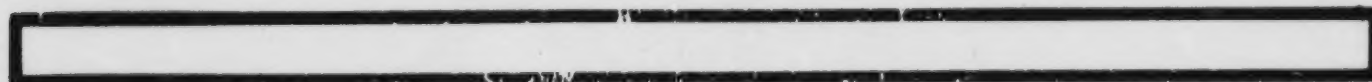
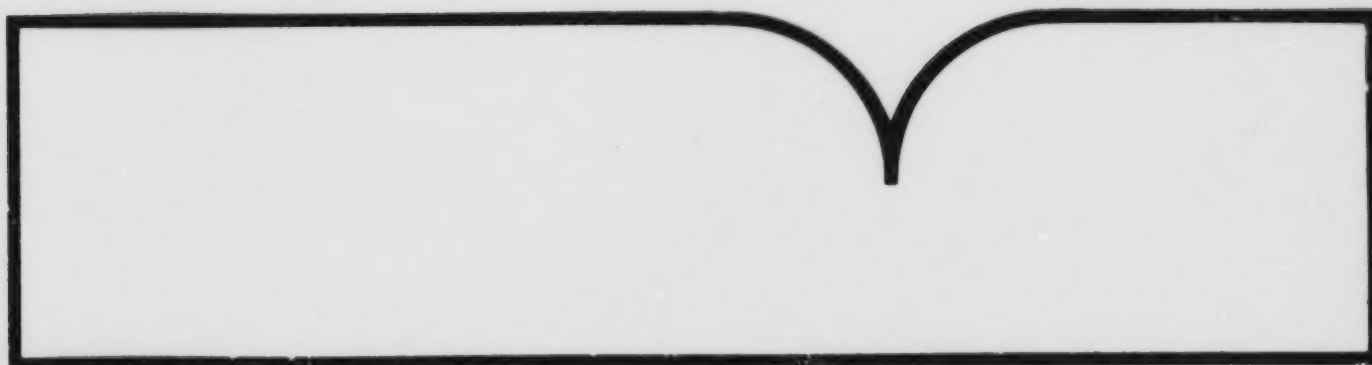
Technology Evaluation for Priority
Pollutant Removal from Dyestuff
Manufacture Wastewaters

Clemson Univ., SC

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Feb 84



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February 1984

TECHNOLOGY EVALUATION
FOR PRIORITY POLLUTANT REMOVAL
FROM DYESTUFF MANUFACTURE WASTEWATERS

by

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Cooperative Agreement No. 807145

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment -- air, water, and land. The Industrial Environmental Research Laboratory contributes to this multidisciplinary focus through programs engaged in

- * studies on the effects of environmental contaminants on the biosphere, and,

- * a search for ways to prevent contamination and to recycle valuable resources.

In this context, this study was conducted to determine the technical feasibility of employing several processes for the treatment of dyestuff manufacture wastewaters, including ozonation, granular activated carbon adsorption, and biophysical (powdered activated carbon/biological, PACT®) treatment. These technologies were evaluated with respect to their capabilities for removing conventional as well as priority pollutants so as to enable the ultimate definition of BAT technologies for the dyestuff manufacturing industry.

David G. Stephan
Director
Industrial Environmental Research
Laboratory
Cincinnati

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ABSTRACT

Laboratory-scale studies were conducted to establish the technical feasibility of employing certain processes, including ozonation, GAC adsorption and biophysical (PACT) treatment, for the treatment of dyestuff manufacture wastewaters with special focus on the removal of organic priority pollutants. The GAC adsorption studies showed that GAC provided for excellent removals of both color and priority pollutants but cannot be expected to concomitantly provide for high levels of SOC removal due to comparatively high levels of non-adsorbable organics that occasionally are present in dyestuff manufacture wastewaters. Excellent removals of organic priority pollutants were achieved by the PACT process. In addition, SOC and color removals were enhanced by the addition of PAC to an activated sludge system, generally in direct relation to the steady-state concentration of PAC in the reactor. Results obtained from the ozonation studies were not as favorable as the results obtained from either the GAC or PACT studies. Although ozonation provided for the removal of many organic priority pollutants to levels below detectability, some proved to be comparatively resistant to oxidation by ozone. As for GAC and the PACT process, ozonation provided excellent color removals. Only moderate organic carbon removals were achieved by ozonolysis, however.

A priority pollutant survey conducted on the influents to and effluents from the wastewater treatment plants (all were activated sludge) of four existing dyestuff manufacturers showed the presence of a total of 23 organic priority pollutants in the raw wastewaters. With the exception of methylene chloride, removal levels of volatile organic priority pollutants generally exceeded 95 percent. Although most acid and base/neutral extractable compounds were removed significantly from the aqueous stream by the activated sludge systems, most compounds were found to be present even after treatment.

This report was submitted in fulfillment of Cooperative Agreement No. 807145 by Clemson University under the sponsorship of the U.S. Environmental Protection Agency. Thus report covers a period from 1 October 1979 to 31 March 1982, and work was completed as of 31 December 1981.

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ACKNOWLEDGMENTS

The cooperation of the Dyes Environmental and Toxicology Organization, Inc. in soliciting member companies to participate in the study is gratefully acknowledged. The assistance and active support provided by the six participating dyestuff manufacturers and their representatives was especially valuable to the conduct and completion of this project. Gratitude is extended to these individuals who shall remain unnamed to protect the anonymity of the participating dyestuff manufacturers.

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SECTION 1

INTRODUCTION

In June 1978, concerned plaintiffs and the Environmental Protection Agency reached a court settlement regarding EPA's alleged failure to implement certain sections of the Federal Water Pollution Control Act of 1972 (PL 92-500). The EPA was ordered to develop a list of toxic pollutants and corresponding effluent limitations based on potential environmental hazard and treatment process capabilities. Following extensive monitoring and toxicity studies, the EPA published a list of 129 priority pollutants that were to be controlled in wastewater treatment plant effluents. The proposed regulation of these pollutants has compelled a number of industries to investigate a variety of treatment technologies that are capable of removing priority pollutants from their wastewaters.

One such industry is the dyestuff manufacturing industry. Previous studies (1) conducted on wastewaters obtained from this industry established that ozonation, adsorption on granular activated carbon, and biophysical (powdered activated carbon/biological, PACT) treatment were well suited for removing conventional pollutants from dyestuff manufacture wastewaters and had significant potential for removing priority pollutants from these wastewaters as well. Accordingly, the principal objectives of the present research program were (i) to exhaustively identify and quantify those priority pollutants contained in dyestuff manufacture wastewaters and to establish the performance characteristics of existing BPT (best practical treatment) with respect to the removal of priority pollutants, and (ii) to affirmatively establish the effect of the three selected candidate BAT (best available treatment) treatment processes on the removal, conversion, and/or production of priority pollutants.

To ensure that the results of this research program were representative of the entire dyestuff manufacturing industry, studies had to be conducted on a representative number of dyestuff manufacture wastewaters. To select those that were to be included in the study, the Dyes Environmental and Toxicology Organization, Inc. was asked to solicit volunteer member companies who would participate. This solicitation resulted in the identification of ten dyestuff manufacturers that indicated a willingness to participate. Because this number was greater than could be accommodated within the budgetary constraints of the cooperative agreement, six dyestuff manufacturers, coded A through F, were selected for participation in the survey. This selection was made on the basis of the following criteria: (i) raw wastewater conventional pollutant characteristics, (ii) treated wastewater conventional pollutant characteristics, (iii) wastewater treatment plant design characteristics, (iv) wastewater treatment plant operational characteristics, (v) class(es) of dyestuffs produced, and (vi) types of non-dyestuff products manufactured.

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The six selected were judged to be the most representative of the entire dyestuff manufacturing industry.

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Moreover, due to budgetary constraints not all of the four constituent studies of this research program could be conducted on each of the six wastewaters obtained from the participating manufacturers. Several of the studies had to be limited to an investigation of less than six wastewaters. The overall experimental program for each wastewater is given in Table 1. Selection was again based on the criteria enumerated above.

TABLE 1. EXPERIMENTAL PROGRAM FOR SIX DYESTUFF MANUFACTURE WASTEWATERS

Component Study	Code for Dyestuff Manufacturer					
	A	B	C	D	E	F
Industry Survey	X	X	X	X	O	O
GAC Adsorption	X	X	X	X	X	X
Biophysical (PACT)	X	X	O	O	O	X
Ozonation	X	X	X	X	X	X

Key: X = Study conducted
O = Study not conducted

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SECTION 2

CONCLUSIONS

Results of an analytical survey conducted on single composite samples of the wastewaters of four dyestuff manufacturers showed the presence of a total of 23 organic priority pollutants in the raw wastewaters. Of these, six were present at concentration levels greater than one milligram per liter. Removal levels of these organic priority pollutants by the activated sludge systems that existed at the sites sampled generally exceeded 95 percent in the case of the volatile organics with the exception of methylene chloride. Although most acid and base/neutral extractable compounds were removed significantly from the aqueous stream by the activated sludge system, many compounds were found to be present even after treatment. Only several of these compounds were present at less-than-detectable concentration levels after treatment.

Analyses for heavy metal pollutants conducted during this survey showed that only minor removals were achieved by the respective activated sludge treatment systems. With the exception of copper, most heavy metals were found to be present in the raw wastewater in the 20 to 200 µg/l concentration range. In two of the three wastewaters sampled, copper was found to be present in the 3 to 6 mg/l concentration range.

Granular activated carbon (GAC) adsorption studies conducted on six dyestuff manufacture wastewaters showed that while excellent removals of both organic priority pollutants and color can be obtained, adsorption of soluble organic carbon (SOC) is not particularly efficient due to the fact that comparatively high concentrations of non-adsorbable organics occasionally are present in these wastewaters. Moreover, it was shown that ozonation pretreatment of these wastewaters generally served to degrade adsorption characteristics.

Parallel PACT (biophysical) and biological (activated sludge) studies conducted on three dyestuff manufacture wastewaters showed that powdered activated carbon (PAC) addition provided for enhanced SOC and color removals, generally in direct relation to the steady-state concentration of PAC in the reactor. Excellent removals of organic priority pollutants were achieved by the PACT system. Heavy metal removal levels were small.

Ozonation studies conducted on six dyestuff manufacture wastewaters showed that ozone provides for excellent color removals but only moderate organic carbon removals as indexed by total organic carbon (TOC). Although many organic priority pollutants were removed to levels below detectability some proved to be comparatively resistant to oxidation by ozone. It was demonstrated, furthermore, that no priority pollutants were produced as a result of ozonation.

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RECOMMENDATIONS

Because the scope of this study was limited to a laboratory-scale evaluation of three wastewater treatment technologies that are especially suited for the removal of organic priority pollutants, no information is yet available regarding the specific operational performance capabilities of these technologies under the dynamical conditions that would be experienced at dyestuff manufacturing facilities. Consequently, a pilot-scale feasibility study should be conducted on-site, at a representative number of dyestuff manufacturing plants to establish the industry-wide treatment capabilities of the three technologies under the dramatic time variant changes in flow and composition that are intrinsic to dyestuff manufacture wastewaters. Upon completion of such a study, a definitive economic analysis of the three technologies should also be conducted.

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SECTION 4

GENERAL METHODS AND MATERIALS

ANALYTICAL METHODS

Organic Carbon

Organic carbon determinations were made using either the direct injection technique with a Beckman (Model 315) Infrared Carbon Analyzer or the ampule technique with an Oceanography International Total Organic Carbon Analyzer. Samples presented to the Beckman Analyzer were acidified with concentrated HCl and purged with nitrogen gas to remove all inorganic carbon. Prior to analyzing a set of samples, the analyzer was calibrated by injecting aliquots of KHP standards using an automatic 20 microliter syringe. A calibration curve was prepared from five replicates of each standard concentration. After calibration, two 20 microliter replicates of each sample were injected. Their average peak height was used in conjunction with the calibration curve to determine the corresponding TOC concentration.

TOC measurements made using the Oceanography International analyzer were made on one milliliter samples contained in ten milliliter glass ampules. One gram of potassium persulfate, five milliliters of distilled water, and 0.2 milliliters of 10 percent phosphoric acid were added to each ampule to aid in oxidation of the organic carbon and to eliminate inorganic carbon. Before sealing, the ampules were purged with oxygen for five minutes to remove inorganic carbon. After oxidation in an autoclave at 103.4 kPa for 15 to 20 minutes, samples first were allowed to cool and then were purged through the infrared analyzer using dried nitrogen gas at 100 milliliters per minute. The area under the response curve was measured by an integrator. Area values were converted to TOC concentration values by means of a calibration curve developed from KHP standards. All samples were analyzed in triplicate and averaged.

Soluble organic carbon (SOC) determinations were made as indicated above with the exception that the samples were filtered through a 0.45 micrometer membrane filter (Millipore Corp.) prior to analysis. Before use the filters were washed individually using approximately 50 milliliters of distilled water to eliminate SOC from detergents that were known to be present.

Color

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Samples were analyzed for color using a technique developed by Wassilak (2), based on the American Dyestuffs Manufacturing Institute (ADMI) weighted

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ordinate method for color value determination. All samples first were filtered through 0.45 micrometer millipore membrane filters to remove suspended and colloidal material and then adjusted to a pH of 7.6 using small quantities 0.025 to 1 N sodium hydroxide or sulfuric acid. Samples were stored in a dark environment at 4°C to minimize photodegradation before color value measurements were made.

The technique involved making absorbance measurements using a Beckman ACTA UV-Visible spectrophotometer. The spectrophotometer was used in double beam operation with distilled water in the reference beam. Settings were slow response, dynode voltage at 360 to 500 volts, and expanded span control. Absorbance measurements were made in the visible wavelength range, 400 to 700 nanometers at 10 nanometer increments to the nearest thousandth of an absorbance unit. The instrument was recalibrated to read zero in the middle of the wavelength span after each 15 samples were analyzed using distilled water in both cells.

Percent transmittance values were calculated from absorbance measurements using the following relation

$$A = 2.0 - \log T$$

where,

A = absorbance unit, dimensionless

T = transmittance, percent.

Using the weighted ordinate procedure outlined by McLaren (3,4), percent transmittance values were used to calculate tristimulus values and subsequently color difference values. The color difference values were compared to a calibration curve of American Public Health Association (APHA) platinum-cobalt color standards. An ADMI color value was subsequently calculated. A computer program developed by Wassilak (2) was employed in these color value determinations. It is to be noted that the accuracy of the ADMI color value technique is unreliable for color values below 50 as determined by Netzer and Miyamoto (5).

Other Conventional Pollutant Parameters

All conventional pollutant analyses not discussed above were conducted in accordance with procedures defined in Standard Methods for the Examination of Water and Wastewater (6).

Heavy Metal Priority Pollutants

All heavy metal analyses were performed in accordance with the EPA manual 600/4-79-020, Method for Chemical Analysis of Water and Wastes (7). The analyses were performed using a Perkin-Elmer Model 403 atomic absorption spectrophotometer that was fitted with a graphite furnace.

Organic Priority Pollutants

All analyses for acid extractable and base/neutral extractable priority

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pollutants were conducted in accordance with EPA Method 625 (8) using a Hewlett Packard Model 5985A Gas Chromatograph/Mass Spectrometer. Due to certain problems that were encountered, two modifications to the procedure were implemented. One modification was necessitated due to the formation of an emulsion when some samples were extracted in a Hershberg-Wolf extraction apparatus. Intermittent stirring of the aqueous/methylene chloride interface with a magnetic stirring bar considerably reduced the build-up of the emulsion in the extractor and prevented trapping of the emulsion in the collection unit.

A second modification was required for quantification of dimethyl phthalate. Because the prescribed specific characteristic ion for dimethyl phthalate (mass 63) produced interferences, a secondary ion with mass 164 was employed for extracted ion current profile (EICP) quantification. All other quantifications were based on the prescribed specific characteristic ion.

Analyses for purgeable organic priority pollutants were conducted in accordance with EPA Method 624 (8) also using a Hewlett Packard Model 5985A GC/MS in conjunction with a Tekmar Liquid Sample Concentrator, Model LSC-2. All samples for analysis of purgeable compounds were collected as grab samples according to procedures defined in Section 5. These samples were composited in the laboratory according to the following procedures. Sample vials and a clean 250 ml round bottom flask were chilled by immersing them in an ice bath. After pouring the entire contents of each vial gently into the flask, the flask was swirled, and composite aliquots for subsequent analysis were poured into precleaned vials. The vials were sealed with zero headspace using TFE-lined septa and screw caps and were stored at 4°C prior to analysis.

Sample foaming, a serious problem of the purge-and-trap method was precluded, by directing a heat gun to the upper portion of the purging vessel. Cross contamination of the purging vessel was avoided by replicate rinsing of the apparatus with organic-free water between samples.

WASTEWATER SAMPLES

All procedures employed for collecting samples for the dyestuff manufacturing industry survey have been defined in Section 5. Samples employed for the treatment technology evaluation studies (Sections 6 to 8) were collected from the equilization basins of the wastewater treatment facilities of the six dyestuff manufacturers that participated in this phase of the study. Approximately 1.51 m³ of wastewater was collected by plant personnel of each participating manufacturer and shipped to Clemson University via motor freight without special precautions during winter months. Shipping time was nominally 10 days. The waste was stored at 4°C and was neutralized immediately prior to use.

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SECTION 5

DYESTUFF MANUFACTURING INDUSTRY SURVEY

INTRODUCTION

Although the primary objective of this study was to establish the technical feasibility of employing granular activated carbon adsorption, ozonation, and the PACT process for the removal of priority pollutants from dyestuff manufacture wastewaters, a study designed to establish the performance characteristics of existing wastewater treatment plants at participating dyestuff manufacturers with respect to the removal, conversion and/or production of priority pollutants was also conducted. This latter study was to serve as a point of reference for the technology evaluation studies described in Sections 6 to 8 of this document.

SURVEY SPECIFIC METHODS, MATERIALS, AND PROCEDURES

All analyses for conventional pollutant parameters as well as heavy metal and organic priority pollutants were conducted in accordance with procedures detailed in Section 4. The protocol that was used for the collection, handling and storage of all samples is reproduced as Exhibit A in Appendix A. This protocol was reviewed and approved by EPA analytical personnel as well as the Project Officer before being implemented at each site in the form of a sample collection, handling, and storage procedures document (Exhibit B, Appendix A).

SURVEY RESULTS

To provide the proper perspective for interpretation of these treatability results, it is important to point out that each of the dyestuff manufacturers that were included in the survey had extensive wastewater treatment facilities. Each had provisions for neutralization followed by a conventional activated sludge system that was coupled with an associated sludge handling train. The activated sludge systems were operated at nominal solids residence times (SRT's) that ranged from 7 to 25 days and hydraulic residence times (HRT's) that ranged from 18 to 36 hours. This configuration and associated operational conditions are relatively typical of the dyestuff manufacturing industry.

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Several of the manufacturers also had adjunct processes such as granular activated carbon adsorption for the liquid processing train. These adjunct processes, however, are not significant to this analytical survey for priority pollutants because all samples that herein are reported as effluent

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samples were collected at the discharge of the solids-liquid separator following the aeration basin and not necessarily at the discharge from the entire wastewater treatment plant. This was done to ensure comparability of the data collected. All influent samples were collected either immediately before or after neutralization depending on which was most feasible at a particular site. More specific details regarding the design and operation of the wastewater treatment processes at each specific site cannot be provided to protect the anonymity of the participating manufacturers.

Results of analyses for conventional pollutants conducted on each wastewater are given in Table 2. These show some significant differences and some commonalities. Of particular note is the fact that the majority (>80%) of the organic carbon present in each of the wastewaters is present in the soluble form. As might be expected the parameter that varies most dramatically from one wastewater to another is color: for example, wastewater Sample B had a color value of 16,700 ADMIU while Sample D had a value of only 1960 ADMIU. It is noteworthy, furthermore, that Samples A and C were collected after neutralization while Samples B and D were collected prior to neutralization.

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Organic Priority Pollutants

The results of all analyses conducted for organic priority pollutants are recorded in Tables 3 through 6 for wastewater Samples A through D, respectively. Of the volatile organic priority pollutants found in the four influent wastewater samples, only chlorobenzene and toluene were found in all four. Ethylbenzene was noted to be present in three of the four samples. All other volatile organics found were present only as single occurrences. Only toluene and ethylbenzene were detected at concentrations greater than the milligram per liter level.

TABLE 2. CONVENTIONAL POLLUTANT CHARACTERISTICS OF FOUR DYESTUFF MANUFACTURE WASTEWATERS

Conventional Pollutant Observed	Wastewater Sample			
	A	B	C	D
TOC (g/m ³)	356	238	411	401
SOC (g/m ³)	315	235	390	320
COD (g/m ³)	1380	760	1870	1080
BOD ₅ (g/m ³)	348	300	520	336
PO ₄ (g/m ³ as P)	5.7	9.1	6.0	6.6
Color (ADMIU)	4760	16,700	4390	1960
pH	7.7	1.9	6.9	2.2
Alk (g/m ³ as CaCO ₃)	155	0	252	0
TSS (g/m ³)	850	216	51	213

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TABLE 3. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE A

Organic Priority Pollutant Observed	Influent (µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
2-Nitrophenol	460	†-	33	55
2,4-Dinitrophenol	2700	-	420	440
Phenol	3200	-	130	190
<u>Base/Neutral Extraction</u>				
1,3-Dichlorobenzene	420	-	3.4	3.7
1,4-Dichlorobenzene	800	-	27	27
Naphthalene	4.0	-	3.9	4.1
Acenaphthene	21	-	4.6	4.9
N-Nitrosodiphenylamine	150	-	4.0	3.6
<u>Volatiles</u>				
Toluene	4000	3600	14	11
Chlorobenzene	180	190	*ND	ND
Ethylbenzene	270	290	ND	ND

*ND means Not Detected (no chromatogram)

† - means not measured

TABLE 4. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE B

Organic Priority Pollutant Observed	Influent (µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
2,4-Dichlorophenol	18	†-	*ND	ND
2,4-Dinitrophenol	5300	-	3900	4700
<u>Base/Neutral Extraction</u>				
1,4-Dichlorobenzene	3200	-	11	13
Nitrobenzene	350	-	91	100
Di-n-butylphthalate	23	-	ND	ND
<u>Volatiles</u>				
Methylene Chloride	5.5	5.5	0.48	0.38
Chloroform	31	33	ND	ND
Toluene	800	780	7.2	7.9
Chlorobenzene	550	550	12	13

*ND means Not Detected (no chromatogram)

† - means not measured

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TABLE 5. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE C

Organic Priority Pollutant Observed	Influent (µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
2-Nitrophenol	7.7	†-	6.6	11.0
Phenol	4900	-	6.7	6.5
<u>Base/Neutral Extraction</u>				
Bis (2-chloroethyl) ether	4700	-	*ND	ND
N-Nitrosodiphenylamine	310	-	ND	ND
<u>Volatiles</u>				
Cis-1,3-Dichloropropene	4.7	5.6	ND	ND
Toluene	160	160	27	19
Chlorobenzene	120	100	ND	ND
Ethylbenzene	4000	4000	ND	ND

*ND means Not Detected (no chromatogram)

† - means not measured

TABLE 6. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE D

Organic Priority Pollutant Observed	Influent (µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
2-Nitrophenol	26	†-	*ND	ND
Phenol	150	-	<20	<20
2,4-Dichlorophenol	††<20	-	<20	<20
<u>Base/Neutral Extraction</u>				
1,3-Dichlorobenzene	18	-	1.2	1.2
1,4-Dichlorobenzene	68	-	4.9	4.9
Nitrobenzene	660	-	2.6	4.3
1,2,4-Trichlorobenzene	230	-	36	37
Naphthalene	120	-	<1.0	<1.0
Phenanthrene	4.5	-	ND	ND
<u>Volatiles</u>				
Carbon Tetrachloride	55	62	ND	ND
1,1,1,-Trichloroethane	220	200	ND	ND
Trans-1,3-Dichloropropene	130	100	2.9	2.5
Toluene	7800	7400	300	270
Chlorobenzene	36	39	ND	ND
Ethylbenzene	67	55	ND	ND

*ND means not detected (no chromatogram)

† - means not measured

†† means a chromatogram was observed, but response was insufficient to quantify

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As expected, removal levels of the volatile organics were very high in the activated sludge systems primarily due to the stripping that occurs as a result of aeration but also due to biodegradation and to adsorption onto the sludge. With the exception of methylene chloride, removal levels generally exceeded 95 percent. Many of the volatile organic materials were removed to levels below detectability.

Of the acid and base/neutral extractable compounds that were found to be present in the influent samples, only phenol, 2,4-Dinitrophenol and Bis (2-chloroethyl) ether were found to be present at concentration levels that exceeded 1 mg/l. Although most acid and base/neutral extractable compounds were removed significantly from the aqueous stream by the activated sludge system, many compounds were found to be present at significant levels even after treatment. This was particularly true in the case of 2,4-Dinitrophenol which was found to be present at a concentration of approximately 4 mg/l after treatment in Wastewater Sample B. Only several compounds were present at less-than-detectable concentration levels after treatment.

Heavy Metal Priority Pollutants

All results for heavy metal determinations conducted on Wastewater Samples A, C, and D are given in Tables 7 through 9, respectively; no analyses were conducted on Sample B. Analysis of this data rather clearly shows that only minor removals of heavy metal priority pollutants were achieved by the respective activated sludge treatment systems. Only in the case of cadmium, copper, antimony and nickel were significant levels of removal achieved, but then only in the case of Wastewater Sample C. On the basis of these results, one may conclude that the removals achieved were not significant.

TABLE 7. HEAVY METAL PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER
ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE A

Heavy Metal Priority Pollutant Observed	Influent (µg/l)	Effluent (µg/l)
Cadmium	22	17
Chromium	142	134
Copper	23	24
Antimony	33	33
Lead	111	66
Nickel	140	102
Zinc	56	56
Thallium	45	<5
Silver	30	15
Arsenic	114	83

means response was observed, but was insufficient to quantify.

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TABLE 8. HEAVY METAL PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER
ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE C

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Heavy Metal Priority Pollutant Observed	Influent ($\mu\text{g/l}$)	Effluent ($\mu\text{g/l}$)
Cadmium	124	28
Chromium	12	12
Copper	3250	82
Antimony	176	59
Lead	*ND	ND
Nickel	160	80
Zinc	14	288
Thallium	ND	ND
Silver	ND	ND
Mercury	3	4
Arsenic	ND	ND
Selenium	20	12

*ND means Not Detected

TABLE 9. HEAVY METAL PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER
ONSITE ACTIVATED SLUDGE TREATMENT FOR SAMPLE D

Heavy Metal Priority Pollutant Observed	Influent ($\mu\text{g/l}$)	Effluent ($\mu\text{g/l}$)
Cadmium	8.7	12.5
Chromium	180	†† <500
Copper	5650	4750
Antimony	200	200
Lead	130	130
Nickel	130	130
Zinc	70	70
Thallium	*ND	125
Silver	ND	ND

*ND means Not Detected

†† means response was observed, but was insufficient to quantify.

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SECTION 6

GAC ADSORPTION TREATMENT TECHNOLOGY

ADSORPTION SPECIFIC METHODS AND MATERIALS

Adsorption Equilibria

Adsorption isotherms were developed using the conventional static bottle technique. This involved placing various selected weights of Calgon Filtrasorb 400 (20 x 30 mesh) into 120 ml French Square bottles and then adding 100 ml of the appropriate wastewater using a volumetric pipet. Prior to use, the granular activated carbon (GAC) was sieved to obtain the appropriate size fraction, washed in distilled/GAC filtered water to remove fines, and dried at 105°C to constant weight. After drying, the GAC was allowed to cool in an open shallow pan for 24 hours such that it equilibrated with the moisture in the atmosphere.

It is important to point out that many researchers typically pulverize the GAC for conducting isotherm studies to significantly decrease the time required for equilibration and to minimize the potential for sample biodegradation. Because Randtke and Snoeyink (9) have shown that this can lead to erroneous isotherm results, the GAC was not pulverized prior to use. To check for sample biodegradation, blank samples were carried through the same procedure used for all other adsorption isotherm samples. No biodegradation was observed throughout all adsorption isotherm studies.

After filling, the isotherm bottles were placed on a New Brunswick Model G10 gyratory shaker which was operated at 200 cpm. The bottles were oriented horizontally to ensure vigorous agitation. All bottles were removed from the shaker after a ten-day equilibration period since it had been demonstrated that adsorption equilibrium was attained in approximately seven days. The contents of each bottle was then filtered through a 0.45 micrometer millipore filter. Aliquots for soluble organic carbon (SOC) analysis were then acidified, using hydrochloric acid, to a pH less than 2 and stored at 4°C in 30 ml screw cap vials until analyzed. Aliquots for color analysis were adjusted to a pH of 7.6 using either sulfuric acid or sodium hydroxide, as appropriate. These samples were also stored at 4°C in 30 ml screw cap vials until analyzed.

Continuous-Flow Studies

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Since this phase of the research also focused on the ability of GAC to remove priority pollutants from dyestuff manufacturers' wastewaters, a continuous-upflow GAC adsorption system was constructed using five columns-in-series. As shown in Figure 1 the columns and their connecting lines were constructed of glass to minimize the adsorption of organics onto column

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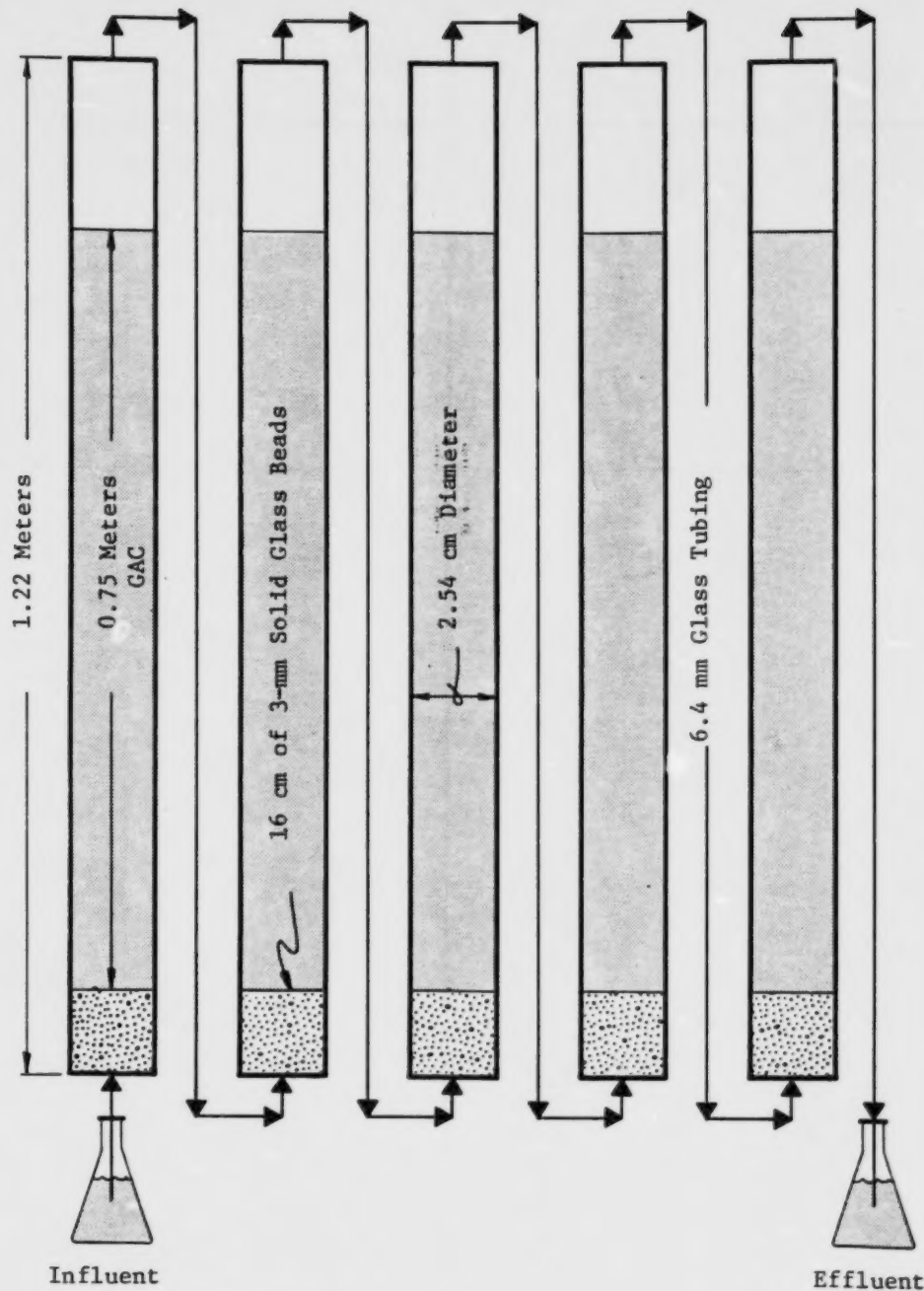


Figure 1. Continuous-flow adsorption column apparatus.

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surfaces. Each column was 1.2 m in length and 2.54 cm in internal diameter. This provided a column to particle diameter ratio of 25:1 which is significantly greater than the 10:1 ratio required to ensure that wall effects are negligible. The inlet section of each column was filled with 3 mm glass beads to a depth of 20 cm to provide for even distribution of flow across the surface of the GAC bed (aspect ratio was 7.9:1). Each column was charged with 203 gm of the 20 x 30 mesh Calgon Filtrasorb 400 GAC. Prior to each run, the GAC was immersed in distilled water for 24 hours to ensure complete wetting of the GAC prior to operation.

These experiments were conducted by passing each of the dyestuff manufacturers' wastewaters through the columnar GAC adsorbers that were charged with virgin GAC. The wastewater was placed in a 50-liter Nalgene carboy that was mixed with air to maintain homogeneity, was allowed to equilibrate at room temperature, was sampled for priority pollutant analysis, and was passed through the GAC columns using a No. 7314 Masterflex peristaltic pump head driven by a Cole Parmer variable speed electric motor. The flow rate through the columns was set at 0.082 m/min (2 gpm/sq ft) which provided an empty bed residence time of 45 minutes for all five columns. The wastewater was pumped through the system to waste for a period of four hydraulic retention times to ensure displacement of the distilled water. Thereafter, the system effluent was collected in a thirteen-liter glass carboy for a period of four hours. at the end of each run conducted on a dyestuff manufacturer's wastewater, the total effluent was mixed and sampled for subsequent priority pollutant analysis.

RESULTS OF ADSORPTION STUDIES

GAC Adsorption Isotherms

Color and SOC adsorption isotherms were developed for wastewaters obtained from all six dyestuff manufacturers. The adsorption equilibrium data obtained using the bottle technique was reduced to determine the quantity of solute adsorbed per unit weight of GAC. This parameter, q , was then plotted as a function of the associated equilibrium concentration of solute remaining in solution, C_e , in the conventional isotherm format which is thermodynamically consistent; some use a log-log transformation which is thermodynamically much less rigorous. The q value was calculated using the following equation:

$$q = \frac{(C_i - C_e)V}{M}$$

where,

q = mass of solute adsorbed per unit weight of GAC (mg/g)

C_i = solute concentration in the blank bottle (mg/l)

C_e = equilibrium solute concentration in the bottle (mg/l)

V^e = volume of wastewater in each bottle (l)

M = weight of GAC in each bottle (g)

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The units given are for the SOC adsorption isotherms. For the color adsorption isotherms, the mass units (mg) are replaced by ADMI color units where appropriate.

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Two series of isotherm studies were performed. One was conducted directly on the wastewater itself while the second was conducted on wastewater samples that had been pretreated by ozonation in an effort to enhance the adsorption characteristics of the organic materials in the wastewater. These latter samples were pretreated at ozone dosage levels that corresponded to those prescribed in Section 8 for the ozonation studies that were designed for priority pollutant removal.

SOC Adsorption -- Adsorption isotherms developed for the six wastewater samples for soluble organic carbon (SOC) are given in Figures 2 through 7 for samples A through F, respectively. The data for both the raw as well as the ozone pretreated samples are given.

Analysis of this data is facilitated by comparison of several adsorption indexes. These include (1) the non-adsorbable fraction obtained by the intersection of the isotherm trace and the abscissa, (2) the GAC solid-phase concentration or "loading" at the operational feed concentration, and (3) the associated calculated GAC exhaustion rate. Values for these parameters are summarized in Table 10.

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TABLE 10. GAC ADSORBER DESIGN FACTORS FOR SOC REMOVAL

Wastewater Sample	Non-Ads. Fraction (g SOC/m ³)	Oper. Feed Conc. (g SOC/m ³)	Ads. Cap. at Feed Conc. (g SOC/kg GAC)	GAC Rate of Exhaustion (kg GAC/1000 m ³)
<u>No Pretreatment</u>				
A	11	160	165	903
B	40	181	165	850
C	75	320	105	2330
D	70	290	175	1260
E	45	445	128	3120
F	590	960	140	2640
<u>Ozone Pretreatment</u>				
A	14	148	100	1340
B	50	189	165	840
C	75	300	87	2590
D	91	300	160	1310
E	22	390	190	1940
F	600	995	135	2930

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When operating prototype or full-scale adsorbers, one would anticipate observing a "bleed-through" concentration of organics equal to, or greater than, the non-adsorbable fraction. Consequently, one can compare the concentration of non-adsorbables with the effluent quality discharge requirements to establish whether or not GAC adsorption is a technically feasible alternative. If the concentration of non-adsorbable organics is greater than the

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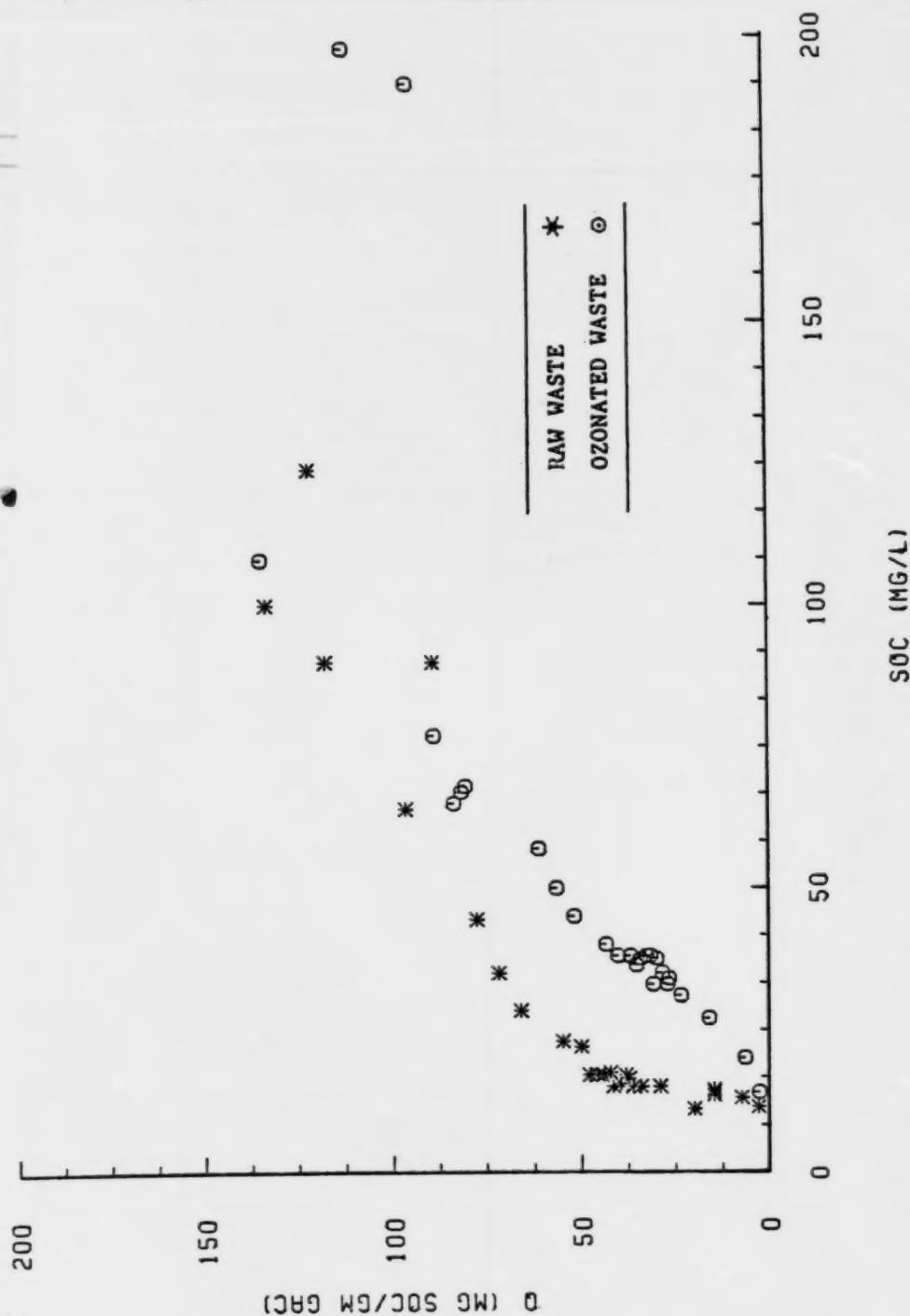


Figure 2. TOC adsorption isotherms for ozonated and non-ozonated sample A.

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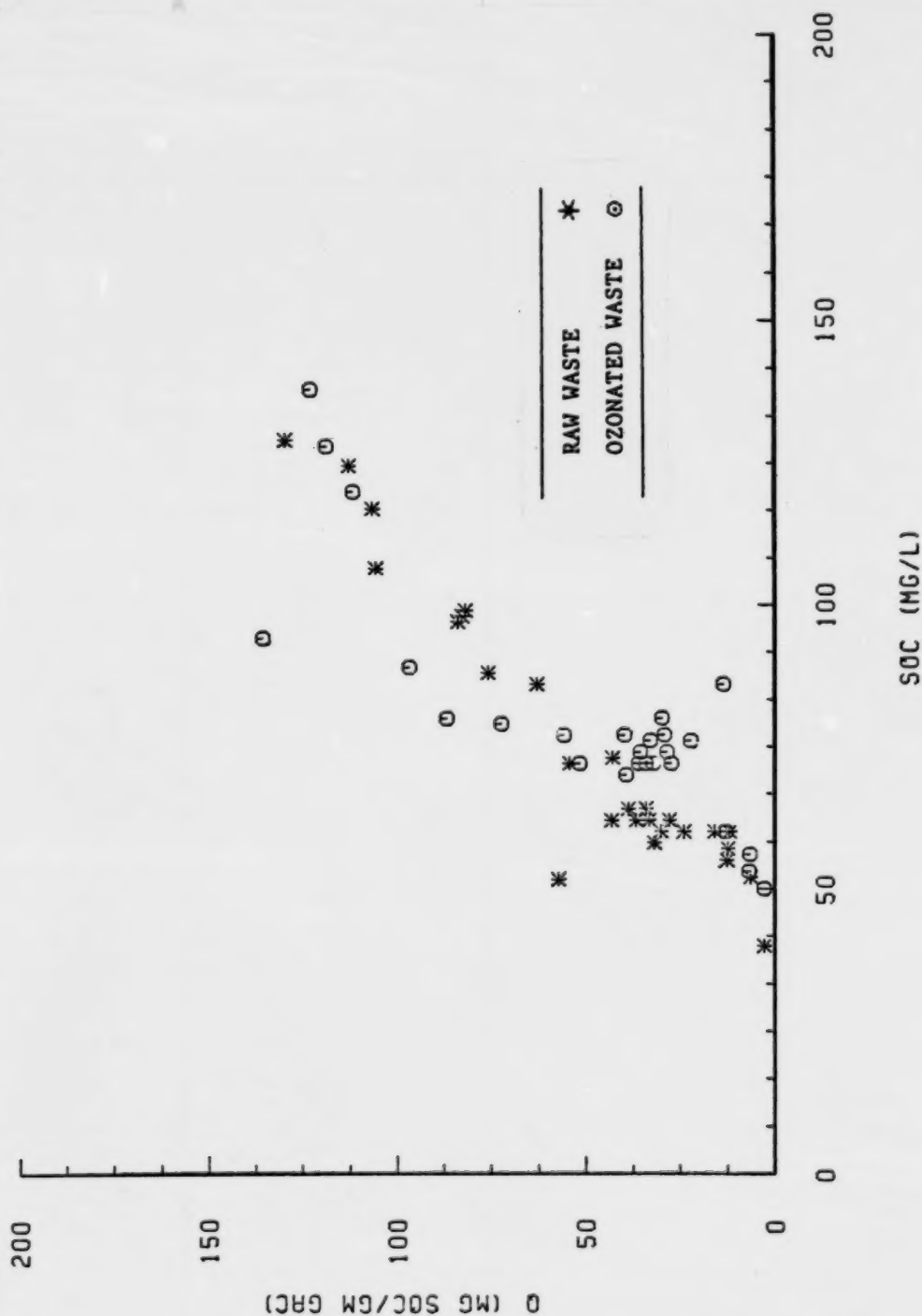


Figure 3. TOC adsorption isotherms for ozonated and non-ozonated sample B.

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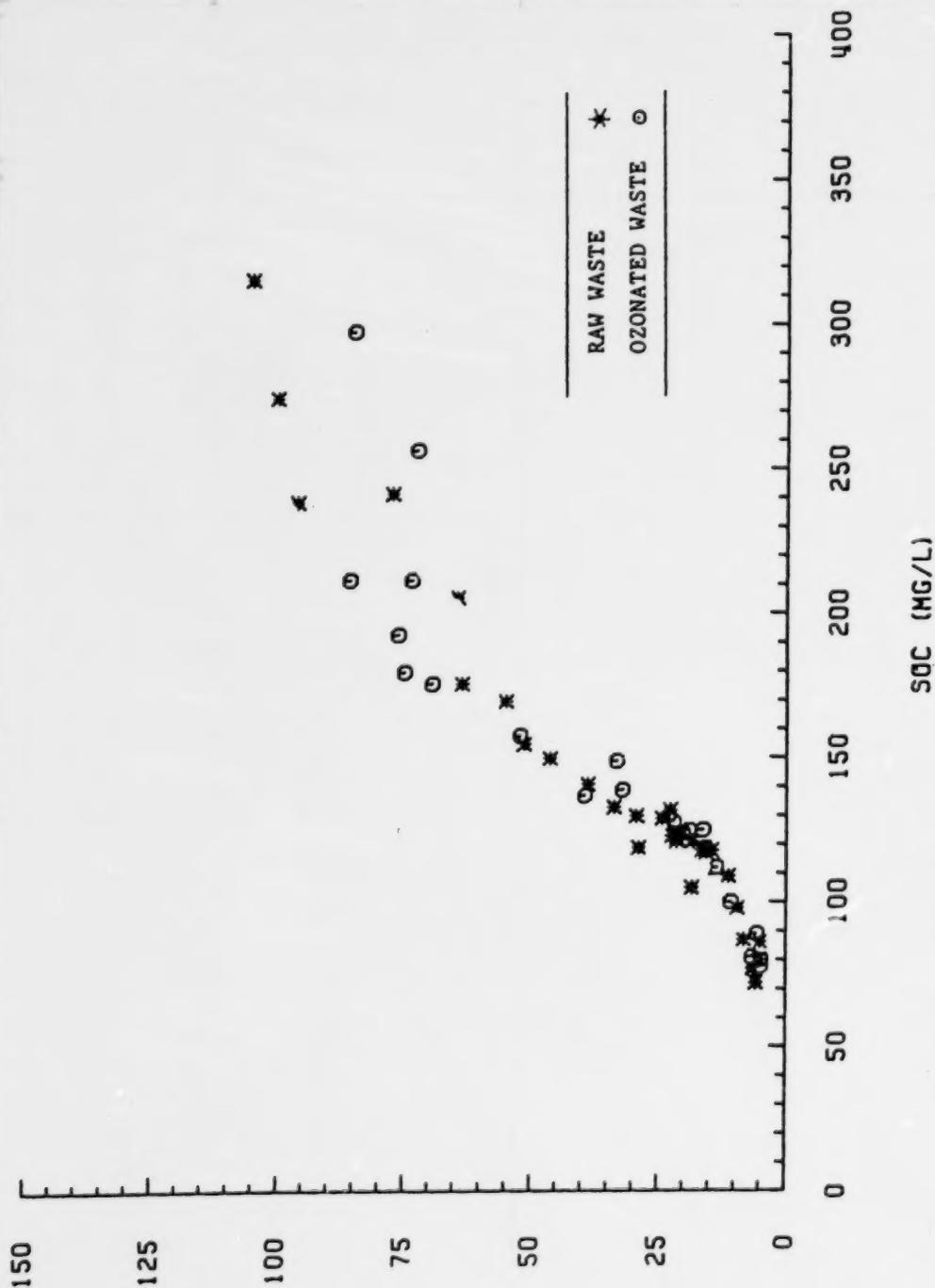


Figure 4. TOC adsorption isotherms for ozonated and non-ozonated sample C.

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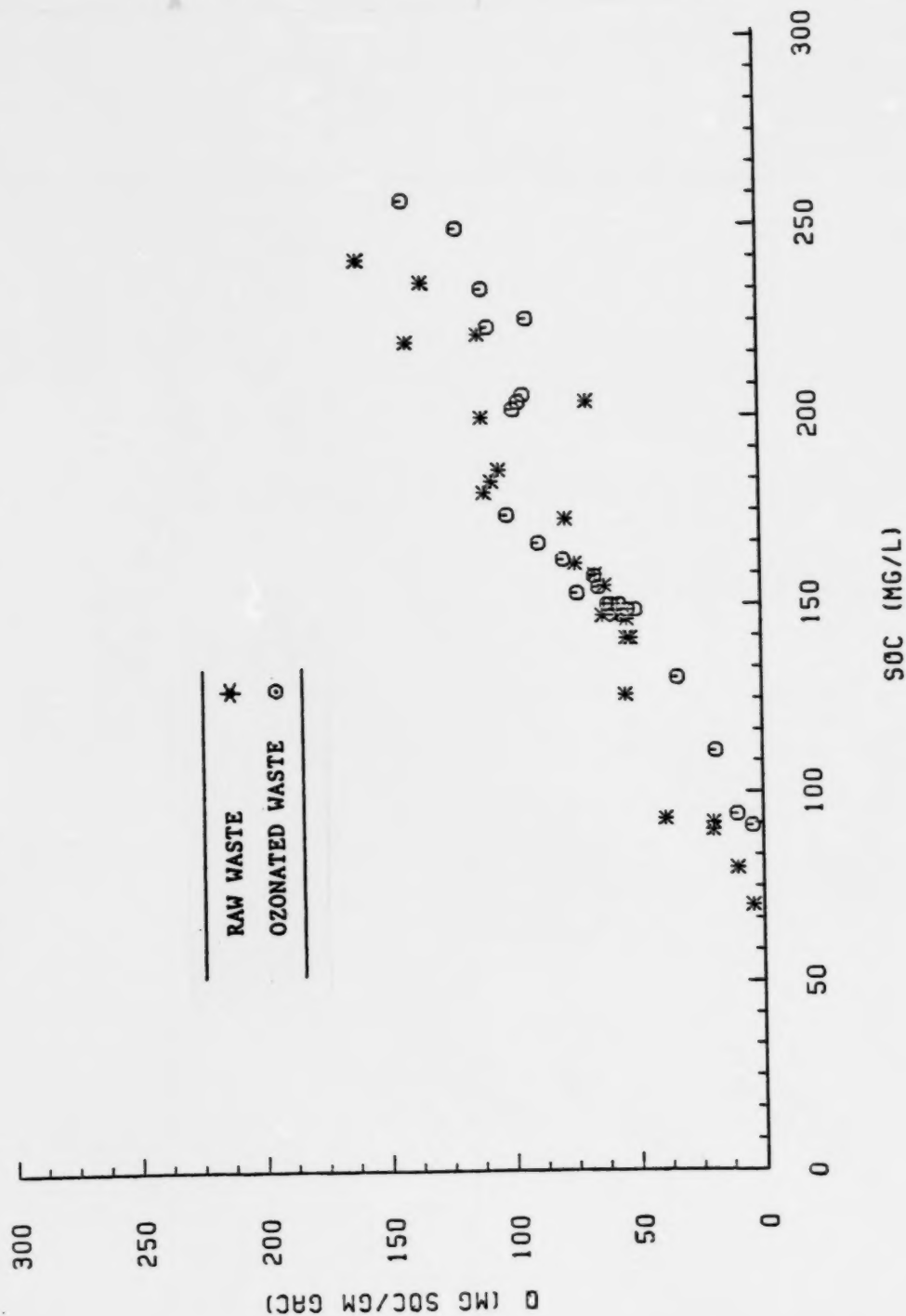


Figure 5. TOC adsorption isotherms for ozonated and non-ozonated sample D.

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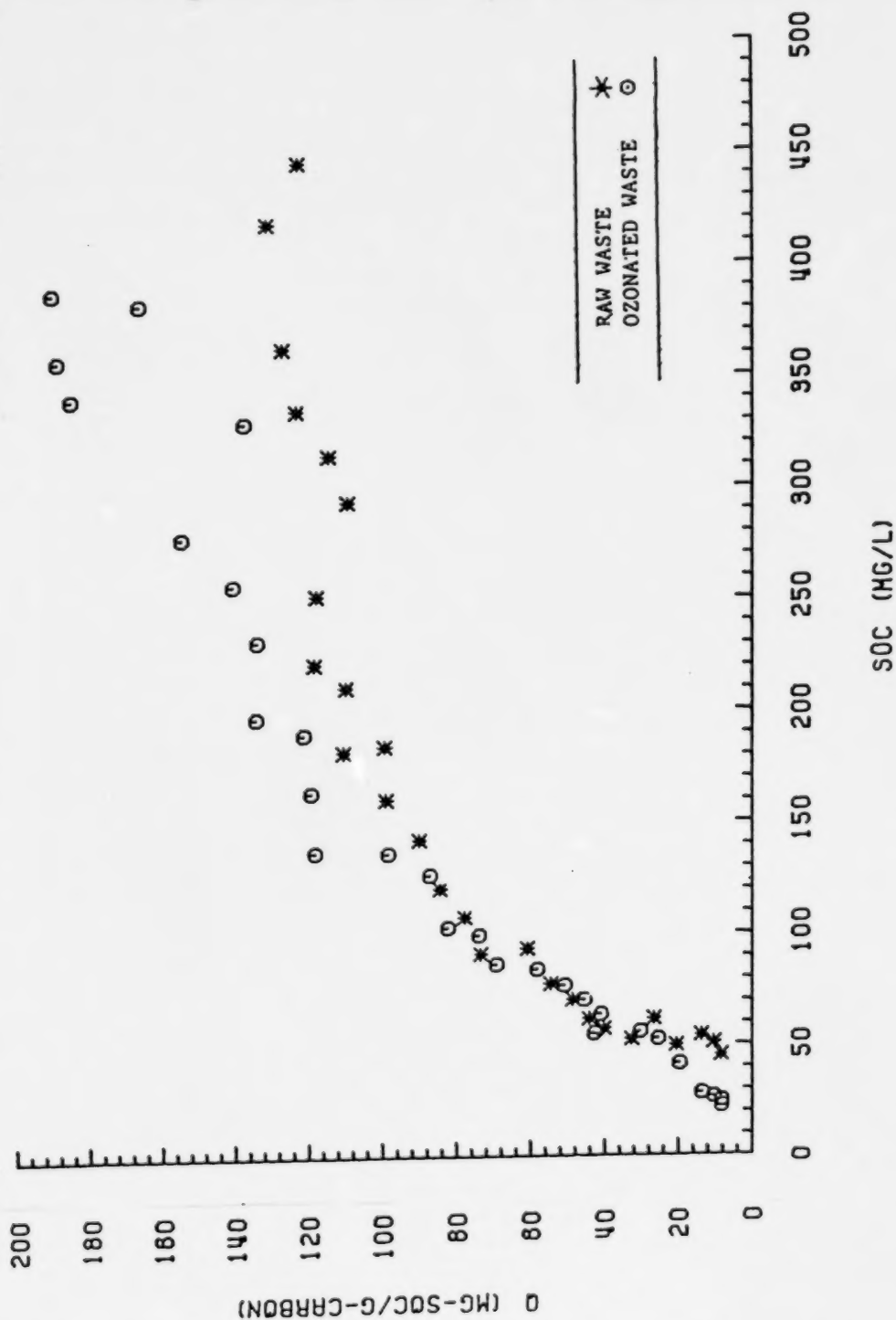


Figure 6. TOC adsorption isotherms for ozonated and non-ozonated sample E.

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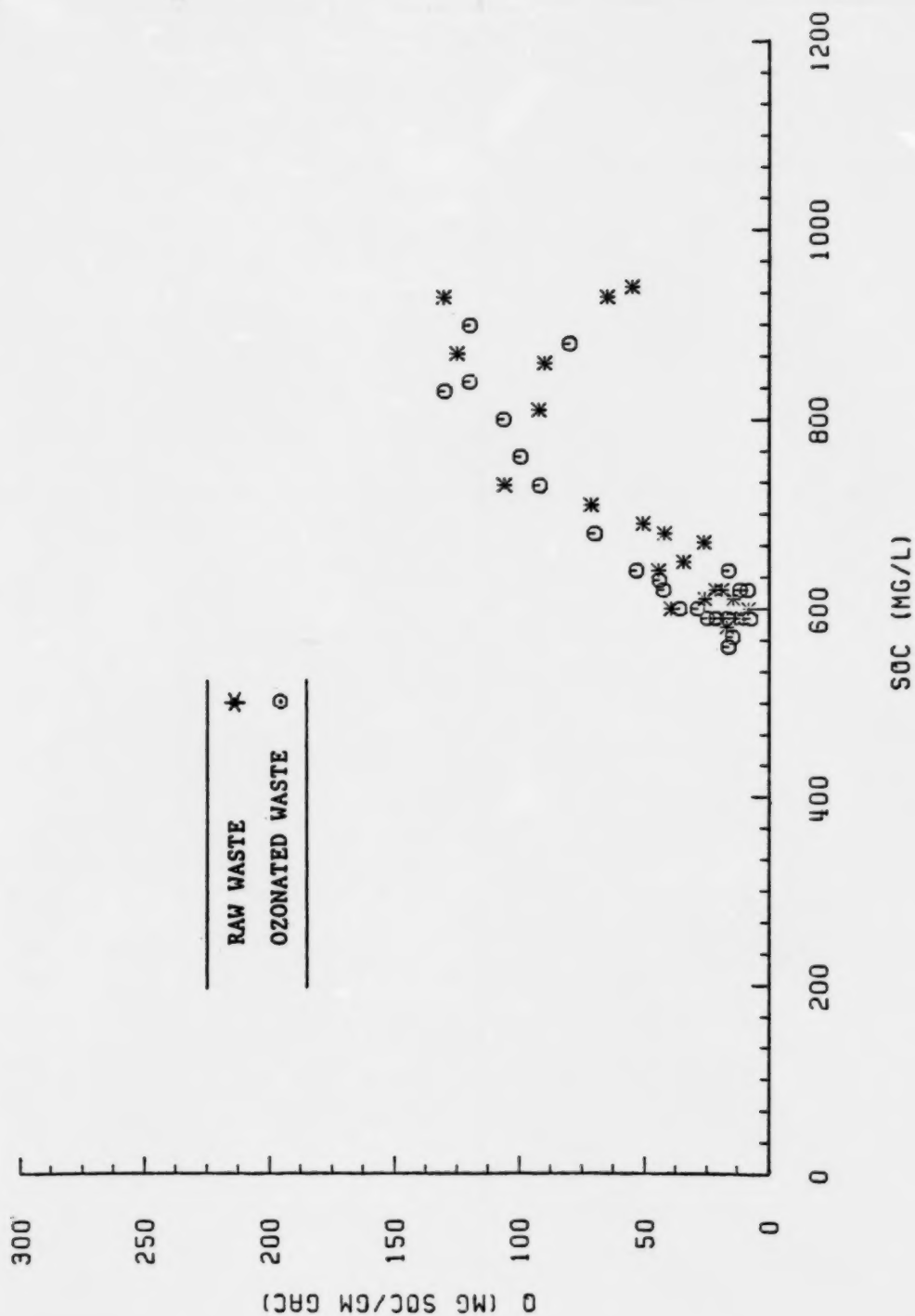
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Figure 7. TOC adsorption isotherms for ozonated and non-ozonated sample F.

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minimum allowable discharge limit for organics, then GAC adsorption is technically infeasible unless some adjunct treatment process can be employed to eliminate or resolve the "bleed-through" problem.

Non-adsorbable organics, usually low molecular weight materials, were present in each of the six raw wastewater samples studied. Significant differences were observed in the level of non-adsorbable organics between the various samples. Samples A through E had non-adsorbable concentrations that ranged from 11 to 75 g SOC/m³, as noted in Table 10. These were in stark contrast to Sample F which had an extremely high non-adsorbable concentration of 590 g SOC/m³. Pretreatment of these wastewater samples served to alter the non-adsorbable fraction of organic materials only slightly. Generally, ozonation led to an increase in the non-adsorbable fraction in all samples with the exception of Sample E.

Calculated GAC exhaustion rates must be indexed to the operational aqueous-phase feed concentration of organics that one would expect to be present in the feed stream to the adsorber. For the present studies, the feed stream concentrations were assumed to be equal to the concentration of organics that existed in the samples either before or after ozonation. These are tabulated in the second column of Table 10, while the associated calculated GAC exhaustion rates are tabulated in the last column. Generally, it is apparent that the GAC exhaustion rates vary rather dramatically from one dyestuff manufacturing wastewater sample to another. In all but two cases, ozonation pretreatment led to an increased GAC exhaustion rate. In the case of Sample B, the slightly lower GAC exhaustion rate was due to the greater non-adsorbable fraction that was present after ozonation. Conversely, the lower GAC exhaustion rate for Sample E was due primarily to the fact that ozonation served to significantly increase the adsorption capacity. This was the only sample for which this observation was made. For all other samples the adsorption capacity either decreased or did not change appreciably.

On the basis of these results it is safe to conclude that ozonation generally has adverse effects on the adsorption characteristics of dyestuff manufacturing wastewaters. This is likely attributable to the following: (i) increased molecular polarity, resulting from the substitution of oxygen into or onto the aromatic rings; (ii) destruction of functional groups which enhance adsorption; (iii) fragmentation of aromatic rings that are capable of forming donor-acceptor (charge transfer) complexes with the GAC surfaces. Nonetheless, because ozonation produced beneficial effects in several cases, it cannot be eliminated from consideration a priori. It should be considered as a potentially viable pretreatment measure for certain applications and should be evaluated as such.

Adsorption of Color -- Adsorption isotherms developed for the six raw wastewater samples for color are given in Figures 8 through 13 for samples A through F, respectively. In addition, color isotherms developed on samples that were pretreated by ozonation are presented along with the corresponding raw wastewater isotherms.

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It is to be noted that GAC capacities for color removal were determined in the usual manner even though color is an intensive rather than a capacitive

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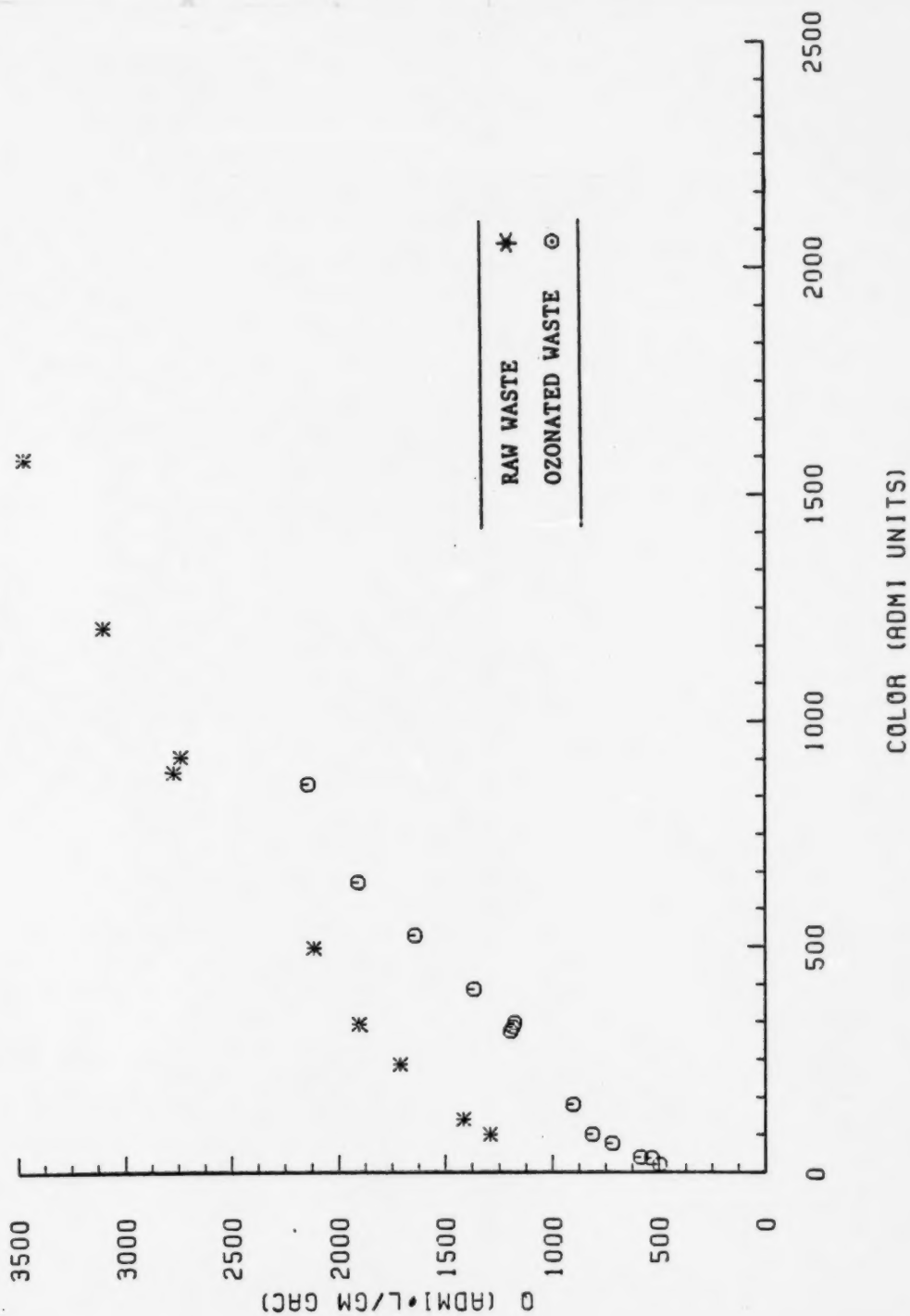


Figure 8. Color adsorption isotherms for ozonated and non-ozonated sample A.

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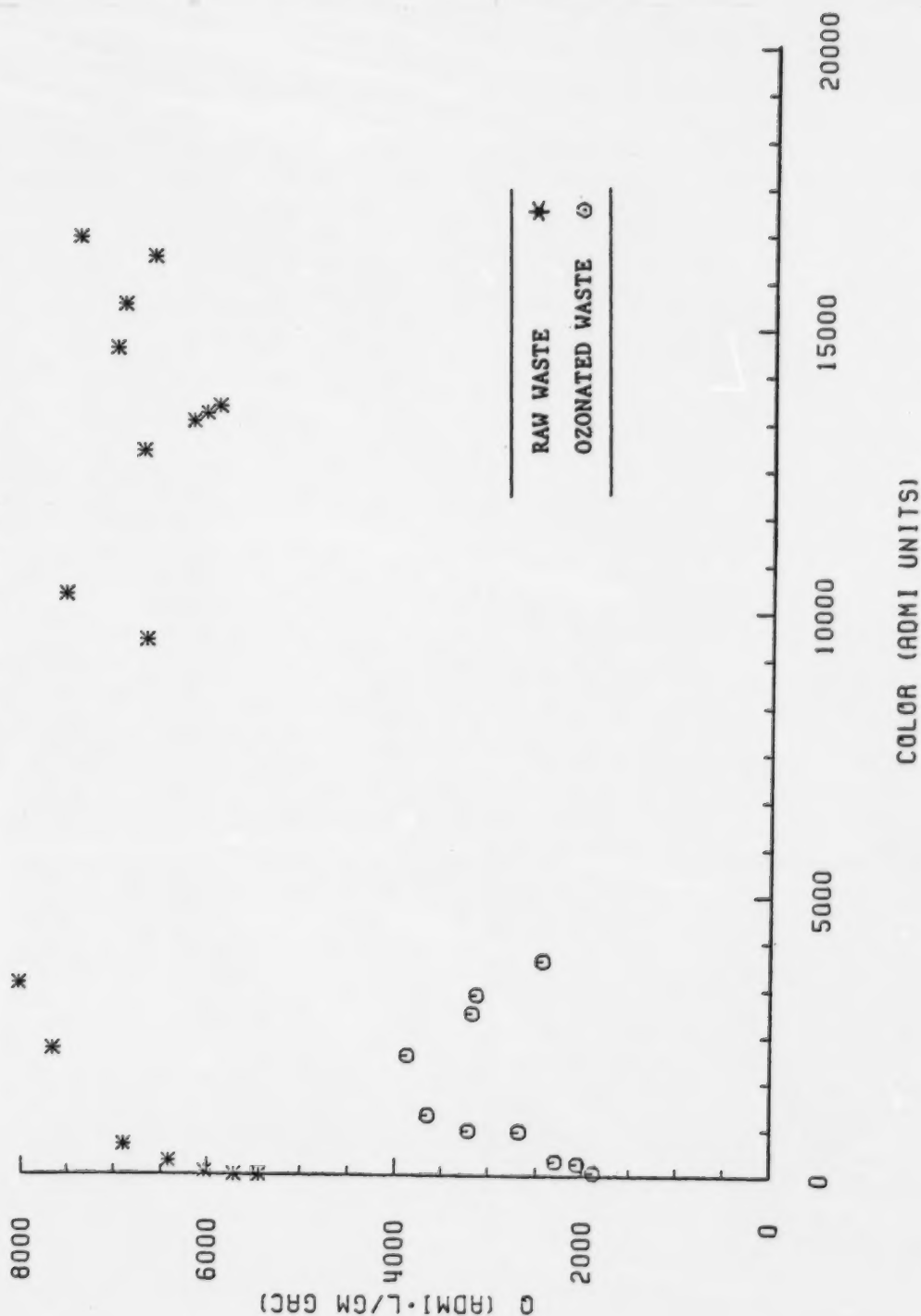


Figure 9. Color adsorption isotherms for ozonated and non-ozonated sample B.

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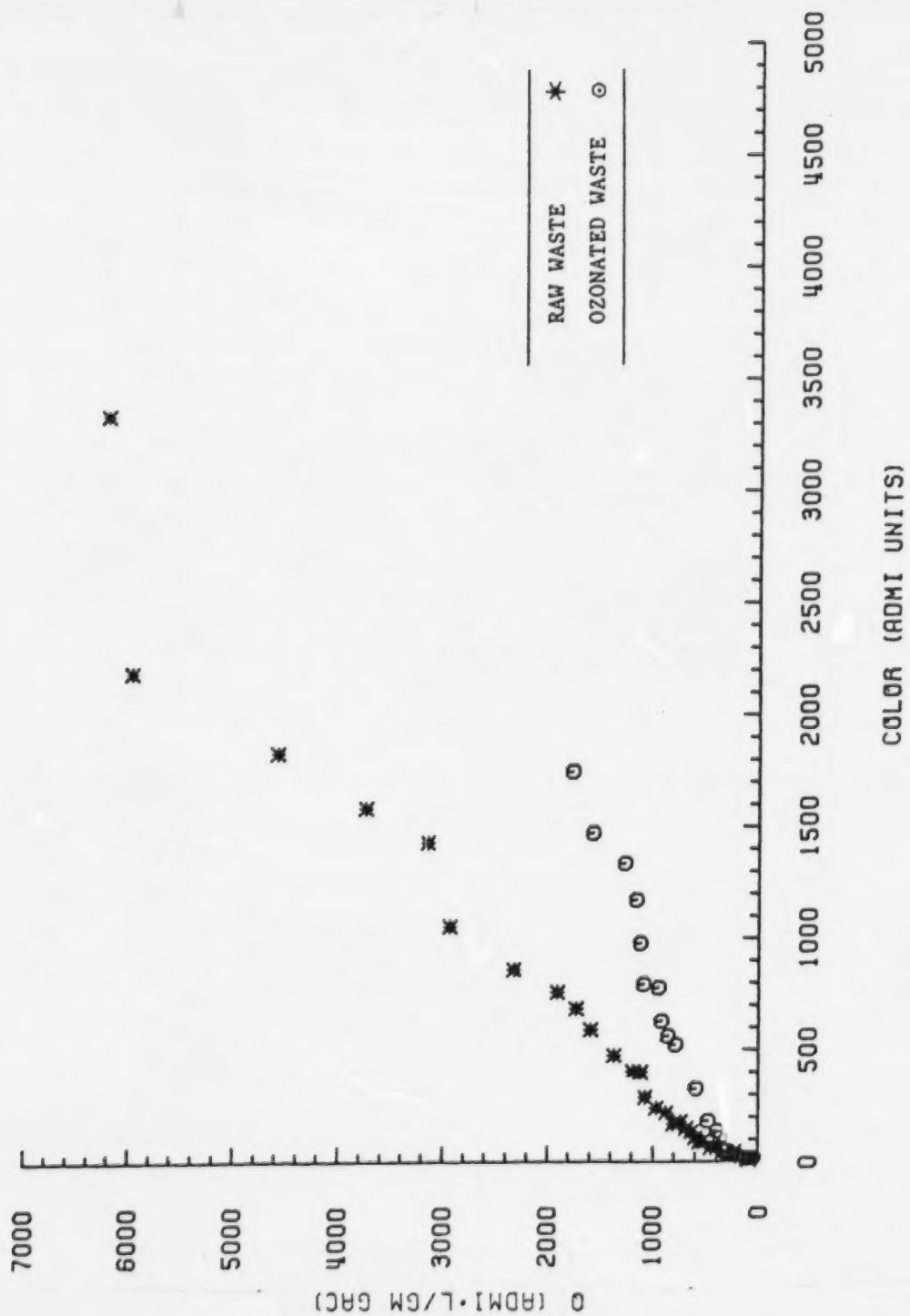


Figure 10. Color adsorption isotherms for ozonated and non-ozonated sample C.

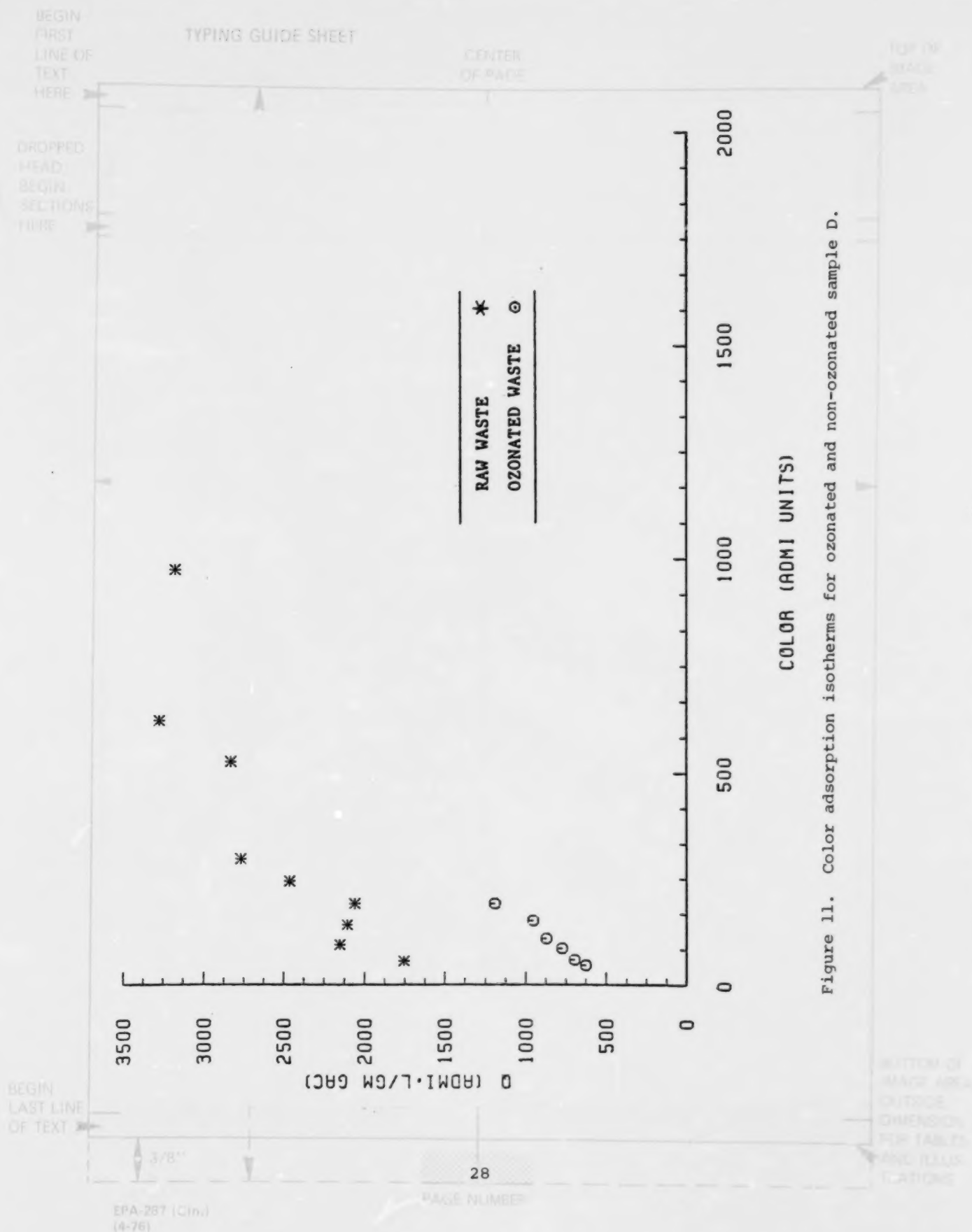


Figure 11. Color adsorption isotherms for ozonated and non-ozonated sample D.

Figure 12. Color adsorption isotherms for ozonated and non-ozonated sample E.

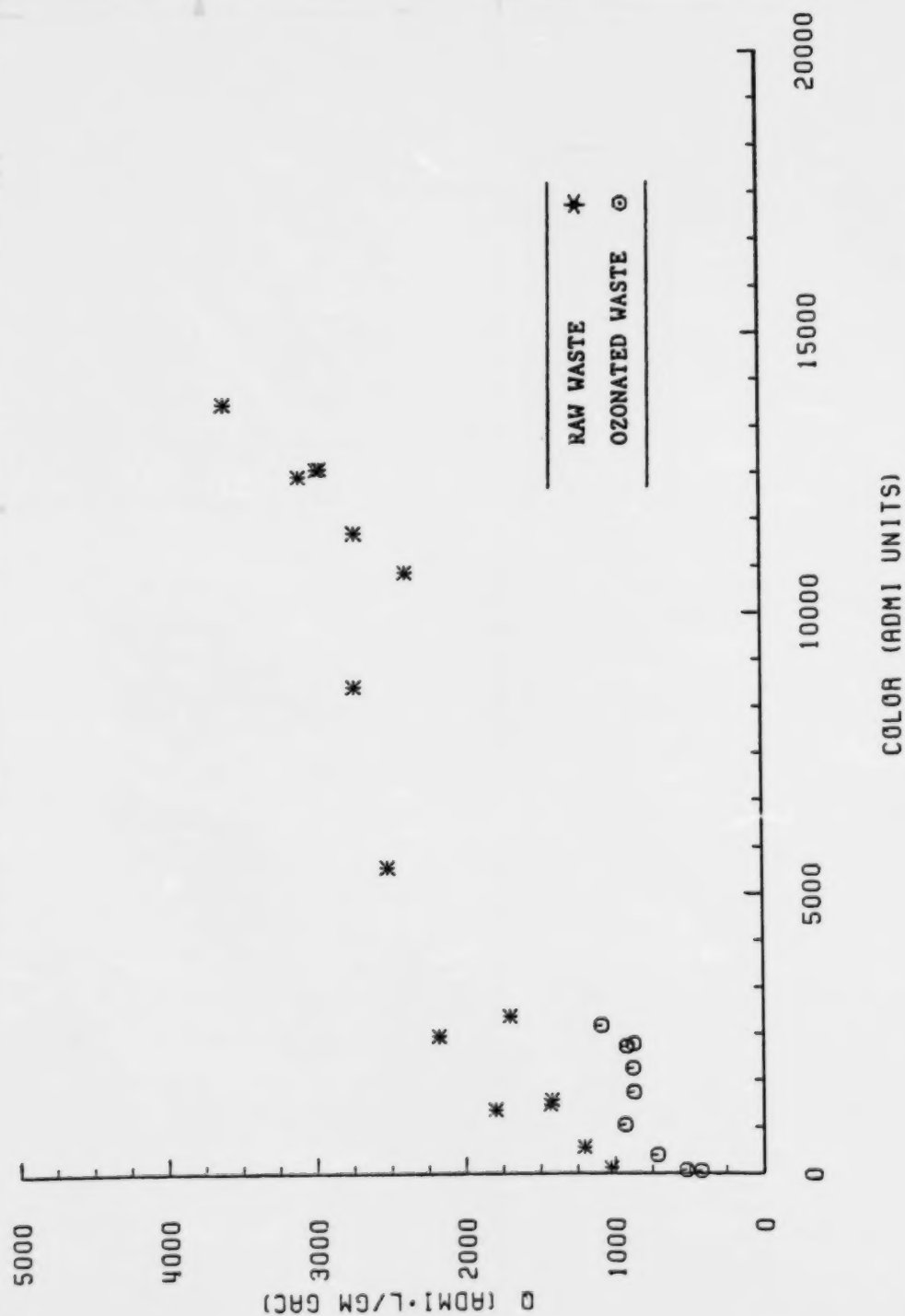


Figure 13. Color adsorption isotherms for ozonated and non-ozonated sample F.

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parameter. Consequently, these color adsorption units (ADMIU - 1/g GAC) can be used only as a measure of adsorbability for comparing different samples and cannot be used for the estimation of design parameters for the sizing of GAC columns. Estimations of these parameters must be obtained from pilot column studies.

Color removal with GAC was very favorable for all wastewater samples. In all cases the isotherms were of a very favorable shape and had no non-adsorbable color. Comparison of the color isotherms again is facilitated by reference to several adsorption indexes given in Table 11. The adsorption capacity at the operational feed concentration (defined previously) varied from 1400 to 7000 ADMIU-1/g GAC. Another parameter that provides an indication of color removal is the mass of GAC exhaustion rate to obtain complete color removal. This index varied from 540 to 5550 kg GAC/1000 m³. It is apparent in these studies, as it was in the prior studies on SOC adsorption, that the adsorption characteristics of Sample F are significantly different than those of the other samples. All other samples were reasonably comparable within the usual expected variations.

TABLE 11. COMPARISON OF COLOR ADSORPTION ISOTHERMS FOR RAW WASTEWATER

Wastewater Sample	Oper. Feed Color Conc. (ADMIU)	Ads. Cap. at Feed Conc. (ADMIU-1/g GAC)	GAC Req'd. for Total Color Removal (kg GAC/1000 m ³)
<u>No Pretreatment</u>			
A	3650	4000	910
B	19500	7000	2790
C	3330	6200	540
D	2250	3300	680
E	3970	1400	2830
F	15500	2800	5550
<u>Ozone Pretreatment</u>			
A	1500	3800	600
B	4840	4000	1210
C	1800	1800	1000
D	549	2400	360
E	2400	990	2520
F	3200	1100	2910

The adsorption isotherms developed for the ozonated samples showed that ozonation pretreatment adversely affected the adsorptive characteristics of the color molecules, although all of the residual color after ozonation remained adsorbable. Nonetheless, because ozonation itself significantly reduced the color level, the combination of ozonation followed by adsorption may indeed be economically viable.

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Priority Pollutant Adsorption Studies

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To establish the technical feasibility of using GAC adsorption for removing organic priority pollutants from dyestuff manufacture wastewaters, a treatability study was conducted on five of the six wastewater samples. These were conducted in accordance with procedures detailed earlier.

The results of these GAC adsorption studies are given in Tables 12 through 16 for the dyestuff manufacture wastewater samples coded A through D and F, respectively. No analyses for volatile organic priority pollutants were conducted in this study. The analytical program was limited to the acid and base/neutral extractable priority pollutant fractions.

TABLE 12. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER GAC TREATMENT OF SAMPLE A

Organic Priority Pollutant Observed	Influent (µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
Phenol	110	120	*ND	ND
2,4-Dinitrophenol	350	340	ND	ND
<u>Base/Neutral Extraction</u>				
2-Nitrophenol	40	35	ND	ND
1,4-Dichlorobenzene	3.4	3.1	ND	ND
Naphthalene	1.6	1.4	ND	ND

*ND means Not Detected

TABLE 13. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER GAC TREATMENT OF SAMPLE B

Organic Priority Pollutant Observed	Influent (µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
2,4-Dichlorophenol	1.3	1.3	*ND	ND
2,4-Dinitrophenol	3200	3300	ND	ND
<u>Base/Neutral Extraction</u>				
1,4-Dichlorobenzene	5.0	6.2	ND	ND
Nitrobenzene	51	47	ND	ND
Di-n-butylphthalate	22	24	ND	ND

*ND means Not Detected

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TABLE 14. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER GAC TREATMENT OF SAMPLE C

Organic Priority Pollutant Observed	Influent (µg/l)	Effluent (µg/l)	
		Dup #1	Dup #2
<u>Acid Extraction</u>			
Phenol	1900	*ND	ND
<u>Base/Neutral Extraction</u>			
Bis (2-chloroethyl) ether	2300	ND	ND
N-Nitrocodiphenylamine	29	ND	ND

*ND means Not Detected

TABLE 15. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER GAC TREATMENT OF SAMPLE D

Organic Priority Pollutant Observed	Influent (µg/l)	Effluent (µg/l)	
		Dup #	Dup #2
<u>Acid Extraction</u>			
Phenol	240	*ND	ND
<u>Base/Neutral Extraction</u>			
1,3-Dichlorobenzene	1.4	ND	ND
1,4-Dichlorobenzene	9.4	ND	ND
Nitrobenzene	830	ND	ND
1,2,3-Trichlorobenzene	8.5	ND	ND
Naphthalene	26	ND	ND

*ND means Not Detected

TABLE 16. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER GAC TREATMENT OF SAMPLE F

Organic Priority Pollutant Observed	Influent µg/l)		Effluent (µg/l)	
	Dup #1	Dup #2	Dup #1	Dup #2
<u>Acid Extraction</u>				
Phenol	57	59	*ND	ND
<u>Base/Neutral Extraction</u>				
Di-n-octylphthalate	1800	1800	ND	ND

*ND means Not Detected

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Results for all samples showed that GAC adsorption effectively removed all of the priority pollutants initially present in the wastewater to below detectable levels, in all cases without exception. The results of these studies are in agreement with similar studies on GAC adsorption of priority pollutants that have appeared in the literature. This is primarily due to the fact that most priority pollutants have very low aqueous solubilities and form good charge transfer complexes with active sites on GAC surfaces. Since these results were achieved for five dyestuff manufacture wastewaters that have widely divergent compositions and matrixes and had widely varying concentrations of priority pollutants, it appears safe to conclude that GAC adsorption appears to be a reasonably universal treatment technology for the removal of organic priority pollutants, neglecting economic considerations. It is important to note, however, that adsorber design criteria were not elaborated by these studies. Such criteria can only be developed by conducting extensive pilot-scale studies.

REACTOR DESIGN AND ASSOCIATED COSTS

To estimate the economic feasibility of employing GAC adsorption for removal of SOC and priority pollutants, it is necessary to design and subsequently develop costs for prototype GAC adsorption systems. Because this is an extremely involved procedure, cost estimates were developed for only two of the dyestuff manufacturers' wastewaters (C and E) as limited surrogates. Four systems were designed and costed for each of these wastewaters: one on the basis of SOC removal and another on the basis of priority pollutant removal -- each at treatment capacity levels of 3780 and 7570 m³/day to investigate the potential benefits associated with economy of scale. In practice, all GAC adsorption systems are designed using pollutant breakthrough profiles obtained from pilot-scale studies. Because this research was limited to the development of isotherm data, the requisite design data, as indicated earlier, was not available. To obtain comparable information, the isotherm data was used in conjunction with a computer program developed by Keinath (10), to simulate the performance of pilot GAC columns. The program thereby allowed the simulation synthesis of breakthrough profiles for pilot-scale columns; thus providing the data normally obtained from pilot-scale adsorption studies.

Simulated SOC breakthrough profiles for the C and E wastewaters were used in conjunction with the Bohart-Adams (11) design procedure to develop a mathematical relationship between breakthrough period and empty-bed residence time. This relationship was then employed to establish the minimum bed residence time required to contain the wave front. Because the minimum acceptable bed residence times so determined resulted in GAC replacement or change-out intervals that ranged from 30 to 80 hours, which are unacceptably short, a 14-day change-out period was selected for design of the required reactor volumes.

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Each GAC adsorption system designed for SOC removal was configured as a parallel system operating in a downflow mode. The design flow and prefabrication limitations determined the number of parallel systems required for each system. The parallel system design consisted of two columns in series, each designed to provide for a 14-day GAC replacement interval.

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Because research by Carpenter (12) showed that the breakthrough of priority pollutants trails SOC breakthrough by a factor as large as five, a 70-day breakthrough period, determined on the basis of SOC removal, was selected for determining the reactor volume required for priority pollutant removal. Of course, it is important to recognize that any adsorption contactor designed for SOC removal would a priori meet the priority pollutant removal criteria.

Due to the fact that the adsorption contactor design volumes were determined on the basis of isotherms that were developed using virgin GAC, the design volumes had to be adjusted to account for the fact that regenerated GAC is commonly used in practice. The minimum required adsorption contactor volumes, therefore, were increased by 25 percent to account for the fact that approximately 20 percent of a virgin GAC's adsorption capacity is lost after several regeneration cycles.

The capital and O&M costs for each GAC adsorption system were estimated using the method presented in EPA's "Process Design Manual for Carbon Adsorption" (13). This cost estimating method made use of cost curves based on design flow, contactor volume, and regeneration furnace capacity. The capacity of the regeneration furnace was designed to be 1.44 times the quantity of GAC exhausted during a breakthrough period. A GAC attrition rate of 10 percent was assumed for estimation of the GAC make-up requirements and a cost of \$0.50 per pound was used to calculate GAC regeneration costs.

The cost curves presented in the EPA manual were updated to 1980 by a ratio of the 1980 cost index to the 1973 cost index. The 1980 value was obtained from a cost index report published by Engineering News Record (14). A ratio of 1.8 was applied to all costs estimated using the EPA cost curves.

The treatment costs determined for these two dyestuff manufacturers, given in Table 17, include amortized capital costs as well as yearly operational and maintenance costs. One may observe that a significant economy of scale exists between the 3780 and 7570 m³/day design flows and that costs for SOC removal were approximately twice those associated with priority pollutant removal.

TABLE 17. PROJECTED GAC SYSTEM TREATMENT COSTS

Dyestuff Manufacturer Code	Treatment Cost (\$/1000m ³)	
	3780m ³ /day	7570m ³ /day
<u>SOC Removal</u>		
C	830	700
E	860	700
<u>Priority Pollutant Removal</u>		
C	420	300
E	390	290

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GAC adsorption studies conducted on six dyestuff manufacture wastewaters showed that while excellent removals of both organic priority pollutants and color can be obtained, adsorption of SOC is not particularly efficient due to the fact that comparatively high concentrations of non-adsorbable organics occasionally are present in these wastewaters. Moreover, it was shown that ozonation pretreatment of these wastewaters generally served to degrade adsorption characteristics. Costs for an adsorption system designed to provide for SOC removal were estimated at approximately \$850 and 700/1000 m³ of wastewater treated at design flows of 3780 and 7570 m³/day, respectively, while costs for priority pollutant removal were estimated at \$400 and 300/1000 m³ for comparable design flows.

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BIOPHYSICAL (PACT) TREATMENT TECHNOLOGY

GENERAL PROCESS DESCRIPTION

Industrial wastewaters, such as those produced by the dyestuff manufacturing industry, may contain compounds which are toxic to microorganisms, compounds which inhibit biological activity, or compounds which are refractory to biological treatment. Combined powdered activated carbon/biodegradation treatment, often termed biophysical treatment, is one relatively new technology that promises to be an economical alternative for removing priority pollutants and inhibitory compounds from industrial wastewaters. This process has been patented by the E. I. duPont de Nemours & Company under the trade name PACT.

A typical schematic flowsheet of the biophysical or PACT treatment system is shown in Figure 14. This treatment system involves the controlled addition of powdered activated carbon (PAC) to the aeration basin of a conventional activated sludge treatment process. The addition of PAC to the aeration basin provides for increased removals of BOD, COD, TOC, color, and toxic compounds, provides for added stability of the biological process, and improves the settling characteristics of the sludge (1). PAC addition also allows for adsorption of organic compounds, provides surfaces for biological attachment, and creates the possibility for the elaboration of beneficial biomass-PAC interactions.

PACT Mechanisms

Presently, much controversy exists concerning the relative significance of the various types of biomass-PAC interactions in PACT systems. The mechanisms by which pollutant removals are increased through PAC addition are not well understood. Removal mechanisms and biomass-PAC interactions in the PACT process are waste specific and must be evaluated on an empirical basis.

In biophysical systems, bacteria, molecules of soluble organics, and oxygen are brought together in close proximity on the surface of the PAC particles. Kalinske (15) has shown that biological oxidation is enhanced by the presence of PAC, perhaps through the provision of a highly localized concentration of substrate and growth sites for the biomass. If PAC acts as a growth site for microorganisms and is capable of uniting the microbial cells and organic substrate at a site thereby causing a higher local substrate concentration, then PAC addition could result in increases in both substrate removal and microbial population. Conversely, if the PAC reduces the available substrate to microbial cells by adsorption, substrate removal

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POWDERED ACTIVATED CARBON

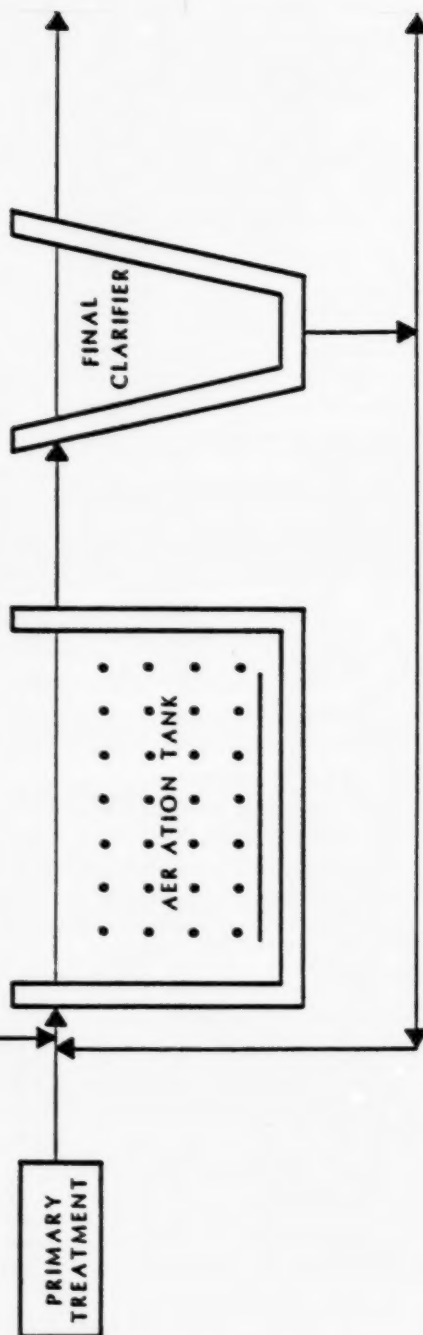


Figure 14. The biophysical (PACT) sytem.

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will be enhanced without any increase in the microbial population. In a study performed by Scaramelli and DiGiano. (16), it was found that biological growth was not enhanced by PAC addition. The enhanced substrate removals that were observed were judged to be the result of adsorption.

Adsorption could also serve to concentrate toxic materials at the carbon surface thus potentially inhibiting biological activity and possibly decreasing the microbial population. Conversely, removal of toxic materials from bulk solution may lead to the enhanced biological degradation of organics.

It has also been suggested that biological assimilation of adsorbed organic material continually frees the carbon surface for further adsorption. This process, known as biological regeneration, has been defined as the ability of microorganisms to utilize adsorbed biodegradable material in such a manner as to renew the adsorptive capacity of the PAC in a biophysical system (17). Sites occupied by readily biodegradable materials are thereby made available for less biodegradable materials. This process is probably controlled by the reversibility of adsorption on PAC surfaces. Results of experiments performed by Flynn, et al. (17) suggest that microorganisms have little ability to directly utilize material that is adsorbed on the PAC.

In contrast, biological growth on PAC surfaces may inhibit adsorption by a blocking of the pores. Robertaccio (18) found that nearly 30 percent of the surface of the PAC that had been in a PACT system for 5 days was inaccessible for adsorption. He also concluded that the ability of microorganisms to utilize adsorbable biodegradable substrate increased in direct proportion to the PAC concentration. This result is probably due to the ability of bacteria to slowly degrade adsorbable organics when they are in contact with the PAC for a period equal to the sludge age rather than the hydraulic residence time.

Accordingly, it is evident that the mechanisms of interaction between the PAC and microorganisms in biophysical systems are not well defined. These interactions are probably dependent on the types of material present in the wastewater and on other factors such as PAC concentration, pH, temperature, and specific operating conditions.

Benefits of PACT Systems

Generally, the PACT process finds utility in (i) upgrading existing activated sludge wastewater treatment plants with a minimum of investment and in (ii) achieving wastewater treatment goals in new plants which cannot be achieved by the activated sludge process alone. Research to date has proven conclusively that the biophysical process achieves higher removal efficiencies than biological treatment.

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Several advantages of PAC addition have been reported. Biophysical systems have been noted to consistently achieve higher BOD, COD, TOC, color and toxic removals when compared to the activated sludge process. They also are more stable in operation and are less adversely affected by changes in flow-rate, feed composition, temperature, pH, and foaming. Robertaccio, et al. (18) reported that experimental PACT systems out perform the conventional

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systems achieving both higher removals and less variability in day-to-day performance even when the PACT systems are operated at half the residence time of the conventional systems.

Bacteria in PACT systems grow around carbon particles in such a manner as to reduce the dispersion of biological flocs thus producing a denser sludge. This sludge settles more readily in the final clarifier, resulting in increased capacities for secondary clarifiers and sludge handling facilities.

PACT processes also offer increased protection for microorganisms from toxic concentrations of adsorbable compounds. Robertaccio *et al.* (18) reported 50 percent removal of lead, zinc, copper, and chromium for the PACT process as compared to 20 to 30 percent removals for the biological process. Similar results have been observed for toxic organic compounds.

Increased nitrification of ammonia to nitrate in municipal wastewater treatment plants using the PACT process has also been reported. Lee and Johnson (19) reported complete nitrification using the PACT system with hydraulic residence times of 3.9, 6.1, and 7.2 hours at temperatures of 10, 8, and 5 degrees C, respectively. Corresponding solids retention times were 12.5, 19, and 39 days. Final effluent $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations were less than 1 mg/l following denitrification. Lee and Johnson (19) also reported reduced sludge bulking for PACT systems.

PACT Control Parameters

Steady state biomass and PAC solids levels in the aeration tank can be controlled by altering the wasting rate and/or the PAC dosage. The solids residence time (SRT) is determined by the wasting rate according to the following relation:

$$\text{SRT} = \frac{\text{biological solids in the system}}{\text{biological solids wasted each day}}$$

SRT affects both the type and quantity of biomass in the system and, consequently, the efficiency of the biological treatment process. The SRT must be sufficiently long to provide adequate time for the generation of the particular biological species that are able to utilize the various substrate components as a source of energy.

Adsorption control is achieved by adjusting the PAC dosage. Increased PAC dosages result in increased treatment efficiencies due to additional adsorption capacity. If PAC regeneration by microorganisms is insignificant, then the virgin PAC concentration is the primary parameter considered when determining requisite PAC dosages. Conversely, whenever biomass-PAC interactions are significant, the existing reactor PAC concentration may be of more importance than the daily PAC dosage. Reactor PAC concentration is also important when considering the settling properties of the sludge.

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Recycle rate is another important control parameter. Recycle rate affects clarification and thickening in the final clarifier, thereby

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effecting the ability of the system to produce an effluent low in suspended solids.

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Because the control parameters are interrelated to some degree, a change in one parameter may affect other control parameters. Daily PAC dosage, (Co), hydraulic residence time (HRT), aeration basin PAC concentration (Ca), and solids residence time (SRT) are related by the following expression:

$$Ca = \frac{Co * SRT}{HRT}$$

It is apparent that a change in the wasting rate would alter the SRT which, in turn, would change the daily PAC dosage required to maintain a desired PAC concentration in the aeration basin. Moreover, if biomass-PAC interactions are significant, any change in PAC concentration or MLSS concentration would affect the substrate removal efficiency.

A low PAC dose, long SRT mode of operation has been demonstrated as a promising method for meeting final effluent limitations (20). This operating mode serves to decrease the operation and maintenance costs by reducing the PAC requirement as well as the required sludge handling capacity.

PAC Regeneration

PAC in the waste sludge can be regenerated by one of several methods. A process developed by Zimpro, Inc. involves partial wet air oxidation of the spent powdered activated carbon and associated organisms. This process oxidizes most of the organisms and adsorbed organic material and leaves the activated carbon intact and renovated for reuse in the biophysical treatment system (21). Multiple hearth incineration has also been used in regenerating spent powdered activated carbon without pyrolyzing the carbon itself. High capital costs and the sophisticated operator technical capabilities required may render PAC regeneration economically unfeasible for small plants.

BIOPHYSICAL SPECIFIC METHODS AND MATERIALS

Wastewater Samples

Due to the fact that experimental evaluation of the biophysical (PACT) process is extremely involved and time consuming, the experimental program was limited to evaluating this process on three dyestuff manufacturers' wastewaters; Samples A, B, and F. These were carefully selected to ensure that the wastewaters generated from the production of three distinctly different product line mixes were evaluated to obtain the broadest-based technology evaluation information possible.

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As indicated earlier, approximately 1.51 m³ of raw wastewater was collected from the equalization basin of each of the three wastewater treatment systems sampled. The waste was stored at 4°C to minimize degradation and was neutralized to pH 7.0. The requisite nutrients, essential for biological growth, were added prior to use as reactor feed. The mass of

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nutrients added was related to the soluble organic carbon (SOC) concentration in the wastewater. The various ratios used are detailed in Table 18. Conventional chemical characteristics of the three wastewater samples are given in Table 19.

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TABLE 18. NUTRIENT SUPPLEMENT RATIOS

Nutrient	Ratio of Soluble Organic Carbon to Nutrient
$(\text{NH}_4)_2\text{HPO}_4$	1.2
FeCl_3	400
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	4
K_2HPO_4	4

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TABLE 19. CONVENTIONAL CHEMICAL CHARACTERISTICS OF WASTEWATER SAMPLES

Parameter	Sample A	Sample B	Sample F
TOC, g/m ³	356	238	1160
SOC, g/m ³	245	235	750
BOD ₅ , g/m ³	348	250	948
COD, g/m ³	1380	760	4200
TSS, g/m ³	850	210	616
PO ₄ , g/m ³ as P	5.7	9.1	9.5
pH	7.5	1.9	9.7
Color, ADMIU	4080	16700	22200

Powdered Activated Carbon

Nuchar S-A 15, manufactured by Westvaco Corporation, was used in this study. A detailed characterization of the PAC is presented as Appendix B. Because this PAC was acid washed during manufacture, it was necessary to wash it prior to use to minimize pH shocks to the biophysical system. Prewashing also removed the PAC fines and produced a more uniform particle size distribution. Due to the fact that biological plate counts showed the presence of significant concentrations of microorganisms in the virgin PAC, the PAC was sterilized in an autoclave prior to use and then stored at 103°C. This eliminated all biological contamination which could have led to the introduction of errors in the experimental studies.

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Daily PAC make-up requirements were supplied to the PACT reactors using an aliquot of a 10 kg/m³ aqueous PAC slurry. Changes in reactor PAC concentration, however, were made by adding a specific weight of dry PAC.

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Biological/Biophysical Reactor System

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An illustration of the laboratory-scale, continuous-flow reactor system is given in Figure 15. The mixed liquor was contained in a glass percolator which was fitted with a diffuser through which compressed air, which has been filtered and humidified, entered the bottom of the reactor vessel. This provided for completely mixed aerobic conditions in the reactor. Exhaust gases were drawn off through a vacuum connection.

Feed solution was supplied to the reactors by a 7014 Masterflex peristaltic pump attached to a Cole Parmer 3200 RPM motor. The wastewater passed from a 20 l plastic feed tank to the reactor vessel through tygon tubing. The contents of the feed tank was mechanically agitated to insure homogeneity of the feed solution. Cam cycle timers were used to aid in control of the flowrate such that low flow rates (2.08 ml/min) could be achieved. The flows to the reactors, therefore, could be controlled both by adjusting the pump's rotational speed and its duration of operation.

Treated wastewater was removed directly from the reactor by a vacuum line connected to a cylindrical vyon cup. Vyon is a porous (15-75 microns) polyethylene material manufactured by Atlas Minerals and Chemicals, Inc. The vyon cups allowed the soluble portion of the treated wastewater to pass into the effluent collection bottles while eliminating most biological solids. This provided for positive control of the biological and PAC solids contained within the reactor.

Reactor Start-Up and Operating Procedures

To determine the effectiveness of the PACT process for treating the dyestuff manufacture wastewaters, two reactors were run in parallel for each of the three wastewaters studied. One system was operated as a conventional activated sludge process and the other, containing PAC, was operated as a PACT system. Both systems were operated at a nominal solids residence time of 20 days and a nominal hydraulic residence time of 24 hours. The HRT and SRT were selected on the basis of previous studies with dyestuff manufacture wastewaters.

Reactor start-up consisted of charging both the biological and biophysical reactors with 3 liters of mixed liquor obtained from the aeration basin of one of the dyestuff manufacturer's activated sludge wastewater treatment facility. An initial aliquot of nutrients was also added to both of the reactors to promote biological growth and to shorten the acclimation period, while an appropriate amount of prewashed, dry, sterilized PAC was added to the biophysical reactor. An initial acclimation period of 40 days was necessary to develop an adequate population of acclimated microorganisms. During this period, the flow rate to the reactors was set to maintain a one-day hydraulic residence time (HRT). Biological and biophysical solids were wasted daily by removing 150 ml of the mixed liquor from each reactor to maintain a solids residence time (SRT) of 20 days. To account for the loss of PAC from the biophysical system due to wasting, an appropriate quantity of virgin PAC was subsequently added to maintain a steady-state PAC concentration in the reactor.

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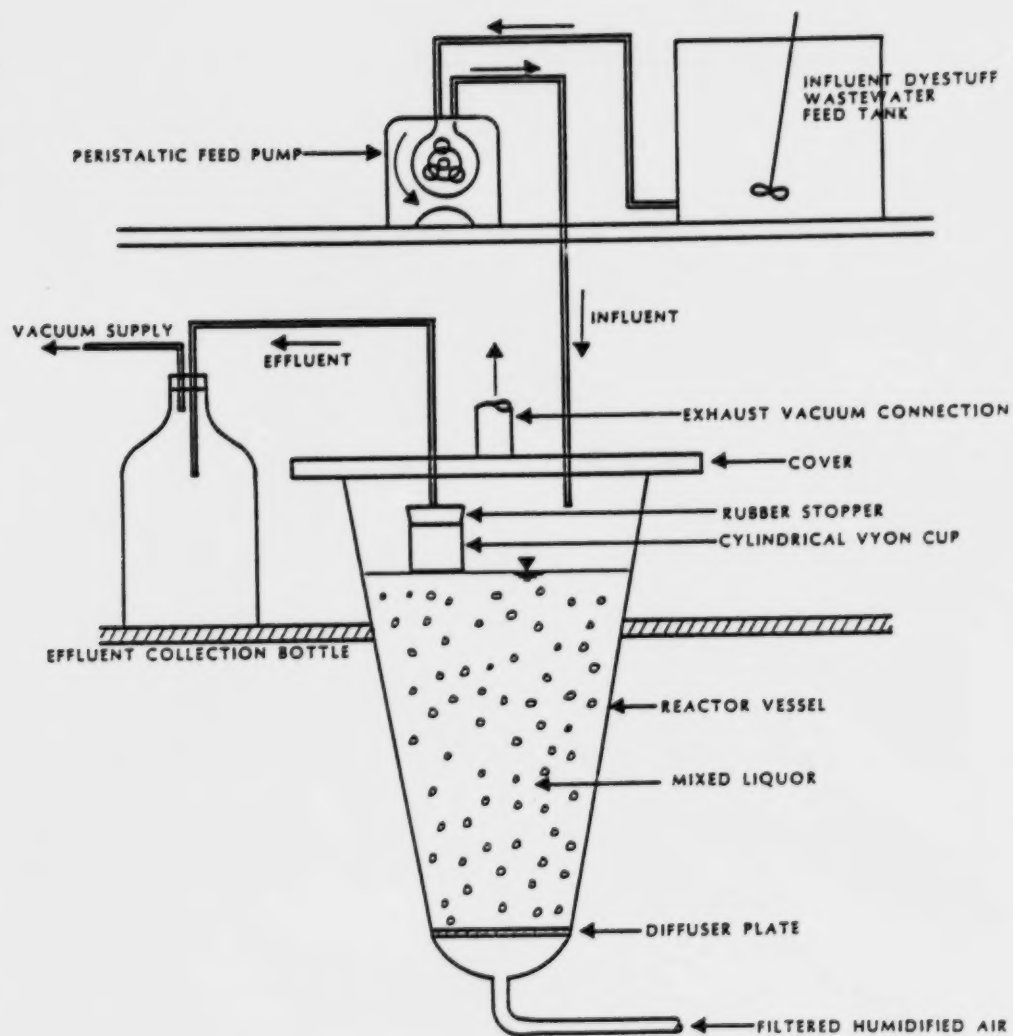


Figure 15. Laboratory-scale, continuous-flow biological reactor system.

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During the acclimation period daily measurements of pH, suspended solids, and soluble organic carbon (SOC) were made to follow the operating conditions of the system. Adjustments in pH were made to maintain the pH of the system in the range of 6.5 to 7.5. The SOC levels in the influent to and the effluent from each reactor were monitored daily to establish the onset of steady-state conditions. Once steady state had been achieved (determined on the basis of SOC analyses), effluent samples were collected from each reactor and analyzed for color, organic priority pollutants, and heavy metals.

Adsorption Isotherms

Adsorption isotherms were conducted in accordance with procedures defined in Section 6 with the exception that the reaction bottles were analyzed after a 2-day period of agitation since adsorption equilibrium was attained within one day.

Analytical Techniques

All analytical techniques were as described in Section 4 with the exception of suspended solids measurements made on mixed liquor samples obtained from the PACT reactor. Two methods were evaluated with respect to their ability to accurately differentiate between biological and PAC solids; the acid digestion technique and the differential temperature technique (19). Preliminary tests showed that the acid digestion technique was unacceptable. The method was abandoned in favor of the differential temperature technique.

The differential temperature technique involves weighing the suspended solids retained on a Whatman GF/F glass fiber filter after drying at 103°C and again after firing in a muffle furnace at 300°C. Biological and PAC solids can then be determined using two coefficients and a set of simultaneous algebraic equations which relate the relative weight loss of biological solids and PAC solids between the two temperatures, 103 and 300°C. The following equations illustrate the calculations required to differentiate PAC and biological solids:

$$X + y = W_{103}$$

$$ax + by = W_{300}$$

where,

$$a = \frac{\text{biological solids remaining @ } 300^{\circ}\text{C}}{\text{biological solids @ } 103^{\circ}\text{C}}$$

$$b = \frac{\text{PAC remaining @ } 300^{\circ}\text{C}}{\text{PAC @ } 103^{\circ}\text{C}}$$

$$x = \text{biological solids concentration, g/m}^3$$

$$y = \text{PAC solids concentration, g/m}^3$$

$$W_{103} = \text{total suspended solids in PACT system at } 103^{\circ}\text{C, g/m}^3$$

$$W_{300} = \text{non-volatile suspended solids in PACT system at } 300^{\circ}\text{C, g/m}^3.$$

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The coefficients a and b were determined by performing the analysis on samples of biological mixed liquor and PAC slurry, respectively. Unfortunately, results from the differential temperature analyses were subject to occasional sporadic errors that were attributable to organic dyestuff solids which were neither biomass nor PAC. Consequently, all PAC solids levels reported were confirmed by mass balance calculation.

RESULTS OF BIOPHYSICAL (PACT) STUDIES

Experimental Strategy

To establish the performance characteristics of the biophysical system, laboratory-scale experiments were conducted on a PACT system in parallel with a control biological reactor. This enabled direct comparison of the PACT and biodegradation processes. Performance evaluations were indexed to four parameters including removal of soluble organic carbon (SOC), removal of color, removal of metallic priority pollutants, and removal of organic priority pollutants.

Adsorption Isotherms

Adsorption isotherms were developed for each of the wastewater samples selected for this study (A, B, and F) using the powdered activated carbon, Westvaco S-A 15.8 This provided a basis for selecting the PAC feed rates and concomitant PAC steady-state concentrations that were to be employed for evaluating the biophysical system. The adsorption isotherms also provided information for interpretation of the resulting data.

SOC adsorption isotherm data for the three wastewater samples were modeled using least squares, Freundlich, and Langmuir linearizations. Using a statistical goodness-of-fit analysis, it was established that the linear least squares model provided the best description of the data for the experimental range studied (PAC dosages of 0 to 9 kg/m³). Linear model parameters for these adsorption isotherms are given in Table 20 along with the calculated concentration of non-adsorbable organic materials which is the equilibrium solution-phase concentration that exists at zero loading. In the case of Samples A and B, the non-adsorbable fraction was approximately 20 percent of the soluble organic carbon present, while the fraction was approximately 40 percent for sample F.

TABLE 20. PARAMETERS FOR LINEAR PAC ISOTHERM MODEL

Wastewater Sample	Intecept (g SOC/g PAC)	Slope (m ³ /g PAC) x10 ⁻⁴	Non-Adsorbable Concentration (g/m ³)
A	-0.0477	8.38	57.0
B	-0.0730	27.72	41.3
C	-0.0875	2.26	386.0

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As indicated earlier, the experimental reactors were operated at a solids residence time of 20 days and a hydraulic residence time of 1 day. Based on the isotherm studies, four PAC reactor concentration levels were selected for experimental evaluation. These were 1, 3, 5, and 7 kg/m³. A parallel or "control" biological reactor that received no PAC feed was operated under identical conditions throughout the duration of the study.

Procedurally, the studies were conducted in order of increasing PAC concentration. Following the completion of a study at one PAC concentration level, the equilibrium PAC concentration was increased by 2 kg/m³ before the system was again allowed to attain a steady-state condition as described previously. This protocol was repeated until all studies for each wastewater had been completed.

Summarized data for these studies is shown in Table 21. Qualitative analysis of the data shows that PAC addition to an activated sludge system appears to enhance system performance and that system performance improved with increasing steady-state concentrations of PAC in the reactor up to 5 kg/m³. Performance did not increase substantially for PAC concentrations greater than 5 kg/m³.

TABLE 21. SOC REMOVALS OBTAINED IN PARALLEL PACT AND BIOLOGICAL REACTOR SYSTEMS

Steady-State PAC Conc. (g/m ³)	Influent SOC Conc. (g/m ³)	Biol. Eff. SOC Conc. (g/m ³)	PACT Eff. SOC Conc. (g/m ³)	Biol. Rem. Efficiency (%)	PACT Rem. Efficiency (%)	Sig. Dif. Between Systems @ 95% Conf. Level
<u>Wastewater Sample A</u>						
1000	250	103	102	58.8	59.2	no
3000	217	99	65	54.5	70.0	yes
5000	236	96	51	59.3	78.4	yes
7000	240	101	49	57.9	79.6	yes
<u>Wastewater Sample B</u>						
1000	164	106	97	35.4	41.0	yes
3000	142	107	68	24.6	52.0	yes
5000	171	105	58	38.6	66.0	yes
7000	157	105	52	33.1	66.7	yes
<u>Wastewater Sample F</u>						
1000	664	380	357	42.8	46.2	no
3000	814	489	433	39.9	46.7	yes
5000	817	352	373	56.9	54.3	no
7000	857	481	389	43.9	54.6	yes

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To provide a more rigorous interpretation of the data, the significance of the differences between the observed removal efficiencies for the PACT and

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activated sludge systems was determined using the "t" statistical test. To do so the variance was calculated for the average percent SOC removed for both the PACT and biological systems. The variances for each of the wastewater samples were pooled. The combined variance was subsequently used for testing the significance of the differences between the removal levels observed for the two systems by means of a t-test.

Reference to the last column of Table 21 shows that, at steady state, the PACT system was statistically more efficient in removing SOC in nine of the 12 experiments conducted. Exceptions were noted for wastewater sample A (PAC level of 1 kg/m³) and wastewater sample F (PAC levels of 1 and 5 kg/m³). In the case of sample F this occurrence is likely due to the fact that a significant quantity of the soluble organic carbon present in the wastewater (ca. 40 percent) is non-adsorbable. Since one of the predominant functional mechanisms of the presence of PAC in a PACT system is simple adsorption, it is obvious that addition of PAC to an activated sludge system would have lesser beneficial effects for wastewaters having greater proportions of non-adsorbable materials.

A statistical analysis was also conducted to establish whether or not significant differences existed in system performance between the various steady-state PAC concentration levels. This analysis, summarized in Table 22, shows that statistically significant differences were observed between PAC concentrations of 1/3 and 3/5 but not for 5/7 kg/m³ for Samples A and B. Because sample F had a comparatively high level of non-adsorbable organics, a significant difference was observed only for the 3/5 kg/m³ PAC concentration pair. On the basis of these results, one may conclude that system performance was not enhanced for PAC concentration levels greater than 5 kg/m³ for the wastewater samples studied.

TABLE 22. STATISTICAL ANALYSIS OF INCREMENTAL LEVELS OF STEADY-STATE PAC CONCENTRATIONS

Steady-State PAC Conc. (g/m ³)	Wastewater Sample		
	A	B	F
1000-3000	yes	yes	no
3000-5000	yes	yes	yes
5000-7000	no	no	no

Color Removal

Color analyses were performed on effluent samples from both the PACT and biological systems as well as the raw feed at each steady-state PAC concentration level. The results of these analyses are given in Table 23. Statistically significant biological removal of color was achieved only for sample A. The removal levels achieved for samples B and F were not found to be

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statistically different than zero. Addition of PAC to the biological reactors proved to significantly enhance color removal levels only for sample A. Only minor increases in color removal were observed for samples B and F as a result of PAC addition.

TABLE 23. COLOR REMOVALS OBTAINED IN PARALLEL PACT AND BIOLOGICAL REACTOR SYSTEMS

Steady-State PAC Conc. (g/m ³)	Influent Color Conc. (ADMIU)	Biol. Eff. Color Conc. (ADMIU)	PACT Eff. Color Conc. (ADMIU)	Biol. Rem. Efficiency (%)	PACT Rem. Efficiency (%)
<u>Wastewater Sample A</u>					
1000	3800	3830	690	0.0	81.8
3000	4350	3810	2530	12.5	41.8
5000	4120	3790	1880	7.9	54.2
7000	4040	3680	1780	9.0	56.3
<u>Wastewater Sample B</u>					
1000	16700	16700	16400	0.1	2.1
3000	17000	16630	15600	2.4	6.2
5000	16900	16900	15200	0.0	10.2
7000	16600	16500	14100	0.8	14.3
<u>Wastewater Sample F</u>					
1000	22200	21800	18900	2.0	15.2
3000	22500	22600	20100	0.0	10.4
5000	22300	20300	20300	8.8	9.1
7000	21700	22100	20200	0.0	6.8

It is interesting to note, furthermore, that color removal levels generally decreased with increasing steady-state PAC concentration levels for samples A and F. Since physical adsorption appears to be the principal mechanism of color removal, this result cannot be rationally explained. The relative removals achieved in the case of sample B are consistent with the anticipated performance.

Removal of Metallic Priority Pollutants

Because one major focus of this investigation was removal of priority pollutants and because the PACT process has been reported to remove heavy metals, heavy metal analyses were performed on filtered raw feed and effluent samples obtained from the PACT system that was operated with a steady-state PAC concentration of 5 kg/m³ and its corresponding parallel biological system. The data from these analyses are shown in Table 24.

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TABLE 24. METALLIC PRIORITY POLLUTANT REMOVALS OBTAINED IN PARALLEL PACT AND BIOLOGICAL REACTOR SYSTEMS

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Metal	Influent Conc. (g/m ³)	Biol. Eff. Conc. (g/m ³)	PACT Eff. Conc. (g/m ³)	Biol. Rem. Efficiency (%)	PACT Rem. Efficiency (%)
<u>Wastewater Sample A</u>					
Ag	0.08	0.06	0.06	25.0	25.0
Cd	0.005	0.005	0.005	0.0	0.0
Cr	0.05	0.05	0.05	0.0	0.0
Cu	0.10	0.48	0.35	*	*
Ni	0.97	0.66	0.59	32.0	39.2
Pb	0.58	0.15	0.15	74.1	74.1
Sb	2.65	2.04	1.21	23.0	54.3
Tl	0.36	0.36	0.47	0.0	*
Zn	0.38	0.66	0.59	*	*
<u>Wastewater Sample B</u>					
Ag	0.04	0.04	0.04	0.0	0.0
Cd	0.005	0.005	0.005	0.0	0.0
Cr	1.50	0.74	0.05	50.7	96.7
Cu	5.71	4.38	1.02	23.3	82.1
Ni	1.09	0.72	0.22	33.9	79.8
Pb	0.15	0.15	0.15	0.0	0.0
Sb	1.21	1.21	1.01	0.0	16.5
Tl	0.12	0.12	0.12	0.0	0.0
Zn	2.60	1.71	0.92	34.2	64.6
<u>Wastewater Sample F</u>					
Ag	0.12	0.12	0.12	0.0	0.0
Cd	0.45	0.21	0.21	53.3	53.3
Cr	3.18	2.84	2.68	10.7	15.7
Cu	55.2	55.4	53.7	*	2.7
Ni	1.65	1.78	2.03	*	*
Pb	0.37	0.30	0.30	18.9	18.9
Sb	2.04	1.94	2.04	4.9	0.0
Tl	0.24	0.24	0.24	0.0	0.0
Zn	0.80	0.54	0.79	32.5	1.2

* negative removal

Analysis of the data shows that it is not particularly conducive to reaching significant conclusions. This is likely due to the fact that the three wastewater matrixes were dramatically different both in the solution- and particulate-phase fractions. Nonetheless, several general observations are appropriate. In the case of sample A, two heavy metals, nickel and antimony, were removed by the PACT at levels that were statistically significantly greater than the removals achieved in the corresponding biological

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control reactor. For sample B, the PACT system performed better for chromium, copper, nickel, antimony and zinc, while the PACT system performed better only in the case of chromium for sample F. The situation is somewhat confused by the fact that the biological control reactor provided better removals of antimony and zinc than did the parallel PACT reactor. On the basis of these results one may conclude that PAC addition to a biological reactor may result in enhanced removals for certain heavy metals, but that the situation is very specific and related to the composition of the aqueous matrix.

Removal of Organic Priority Pollutants

To establish the technical feasibility of using PACT systems for providing for the removal of organic priority pollutants from dyestuff manufacture wastewaters, analyses for organic priority pollutants were performed on composite samples obtained from the feed and the effluent of the PACT system that was operated with a steady-state concentration of PAC of 5 kg/m³. The data from these analyses are shown in Table 25.

TABLE 25. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS BEFORE AND AFTER PACT TREATMENT

Organic Priority Pollutant Observed	Influent (µg/l)	Effluent (µg/l)	
		Dup #1	Dup #2
<u>Wastewater Sample A</u>			
2-Nitrophenol	570	*ND	ND
Phenol	4400	ND	ND
2,4-Dichlorophenol	2500	ND	ND
1,4-Dichlorophenol	65	ND	ND
1,3-Dichlorobenzene	12	ND	ND
Acenaphthene	40	ND	ND
N-Nitrosodiphenylamine	32	ND	ND
<u>Wastewater Sample B</u>			
2,4-Dinitrophenol	2500	ND	ND
Phenol	5300	8.5	7.7
1,4-Dichlorobenzene	77	ND	ND
Nitrobenzene	120	ND	ND
Fluoranthene	13	ND	ND
<u>Wastewater Sample F</u>			
Bis (2-ethylhexyl) phthalate	560	ND	ND
Di-n-octyl phthalate	1200	ND	ND

*ND means Not Detected

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The results for all samples showed that the PACT system effectively removed all of the organic priority pollutants initially present in the wastewaters to below detectable levels, with a single exception. This was in the case of phenol that was present in Sample B at a level of 5300 $\mu\text{g/l}$. An average residual level of 8.1 $\mu\text{g/l}$ was observed to be present after PACT treatment. This represents a treatment efficiency in excess of 99.8 percent. Had a similar analyses been performed on a composite sample obtained from the PACT reactor that was operated with a steady-state PAC concentration of 7 kg/m^3 it is probable that the phenol in this sample would also have been decreased to a concentration level that was less than detectable.

Since these results were obtained for three dyestuff manufacturing wastewaters that have widely divergent compositions and matrixes and widely varying concentrations of priority pollutants, it is reasonable to conclude that the PACT process is effective for the removal of organic priority pollutants.

SUMMARY

Parallel PACT (biophysical) and biological (activated sludge) studies conducted on three dyestuff manufacture wastewaters showed that PAC addition provided for enhanced SOC and color removals, generally in direct relation to the steady-state concentration of PAC in the reactor. It was also shown, however, that whenever the wastewater has a significant non-adsorbable fraction, PAC addition provides for incrementally smaller removals. Excellent removals of organic priority pollutants were achieved in the PACT system. Removals of heavy metal priority pollutants were small and differed significantly from one wastewater to another.

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SECTION 8

OZONATION TREATMENT TECHNOLOGY

OZONE AS A CHEMICAL OXIDANT

Physical Characteristics

Ozone is an allotrope of oxygen containing three oxygen atoms in a state of resonance. As an allotrope, it is able to react as an electrophile, nucleophile, or 1,3 dipole as stated by Evans (22). The physical characteristics of ozone are presented in Table 26 (23).

TABLE 26. PHYSICAL CHARACTERISTICS OF OZONE

Characteristic	Value
Molecular Weight	48 gm/gm-mole
Formation	Photochemical reaction or Electrical discharge
Specific Gravity (air=1)	1.658
Weight (0°C and 1 atm)	2.144 g/l
Solubility in water	1.09 g/l (0°C); 0.57 g/l (20°C)
Melting Point	-251°C
Boiling Point	-112°C
Oxidizing Potential	-2.07 V
Absorption Wavelength	2537 angstroms
Color	None at low concentrations
Odor	Pungent, fresh <5 ppm; Obnoxious, acrid >5 ppm
Toxicity	Yes

Ozone is an extremely unstable gas with a reported half-life of 0.5 to 41 minutes in distilled water, depending on pH. The influence of pH on ozone half-life is shown in Table 27. Ozone decomposition rates in wastewater were shown by Hewes and Davison (24) to be 2nd order at pH 2 and 4, 3/2 to 2nd at pH 6, and 1st order at pH 8. Above pH 6, the decomposition rate increases rapidly with pH.

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TABLE 27. OZONE HALF-LIVES AT VARIOUS pH VALUES (after Stumm, 25)

pH	Half-life (minutes)
7.6	41
8.5	11
8.9	7
9.2	4
9.7	2
10.4	0.5

Overview of Reaction Pathways and Products

Ozone can react by several mechanisms, occasionally by more than one at the same time. This was postulated by Maggiolo (26) who stated that mechanism type depends upon pH, the presence of metals, and the types and relative concentration of organic compounds present. Two principal reaction mechanisms of ozone with wastewater compounds are known to occur: ionic and a free radical.

The reaction of ozone with organics is dependent primarily on bond type and structure. Bailey (25) has stated that carbon-carbon and carbon-nitrogen double bonds are the most reactive with ozone. The classic reaction of ozone with a carbon-carbon double bond (ozonolysis) was first described by Crigee (28) as shown in Figure 16. The initial attack by ozone occurs as a 1,3 cyclo-addition. This produces a five-membered ring called a 1,2,3-trioxolane which is broken down into the Crigee zwitterion and a by-product. The important intermediate in the model is the zwitterion which is extremely unstable and must react either with the ketone or aldehyde formed or with water to produce the end products. Some modifications to Crigee's proposed reaction have been made, but the basic concept he presented is still widely accepted.

Ozone is also reactive with most aromatic compounds, although slower than its reaction with alkenes. Ozonation of aromatic compounds involves both ozonolysis at the most reactive double bond and an electrophillic attack at individual carbon atoms. Electron deficient groups, such as the nitro, sulfonic acid, carbonyl, and halogens slow down the rate of ozone attack on the ring structure. Electron releasing substituents, such as the alkyl, methyl, and hydroxyl groups activate the ring toward ozone. For example, increasing methyl groups on a benzene ring increases the reactivity with ozone as shown by Oehlschlaeger (29). Ozonolysis products of the various aromatic compounds (30, 31, 32, and 33) include alcohols, aldehydes, ketones, peracids, ozonides, and epoxides.

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Aromatic heterocyclic compounds are also reactive with ozone, an exception being pyridine which contains a stable ring structure. Reaction mechanisms include a 1,3-dipolar cyclo-addition of double bonds and an electrophillic attack at individual carbon atoms. Ozonolysis of aromatic heterocyclic compounds forms aromatic aldehydic and acidic derivatives. Simple heterocyclics such as pyroles and furans are readily attacked and have the

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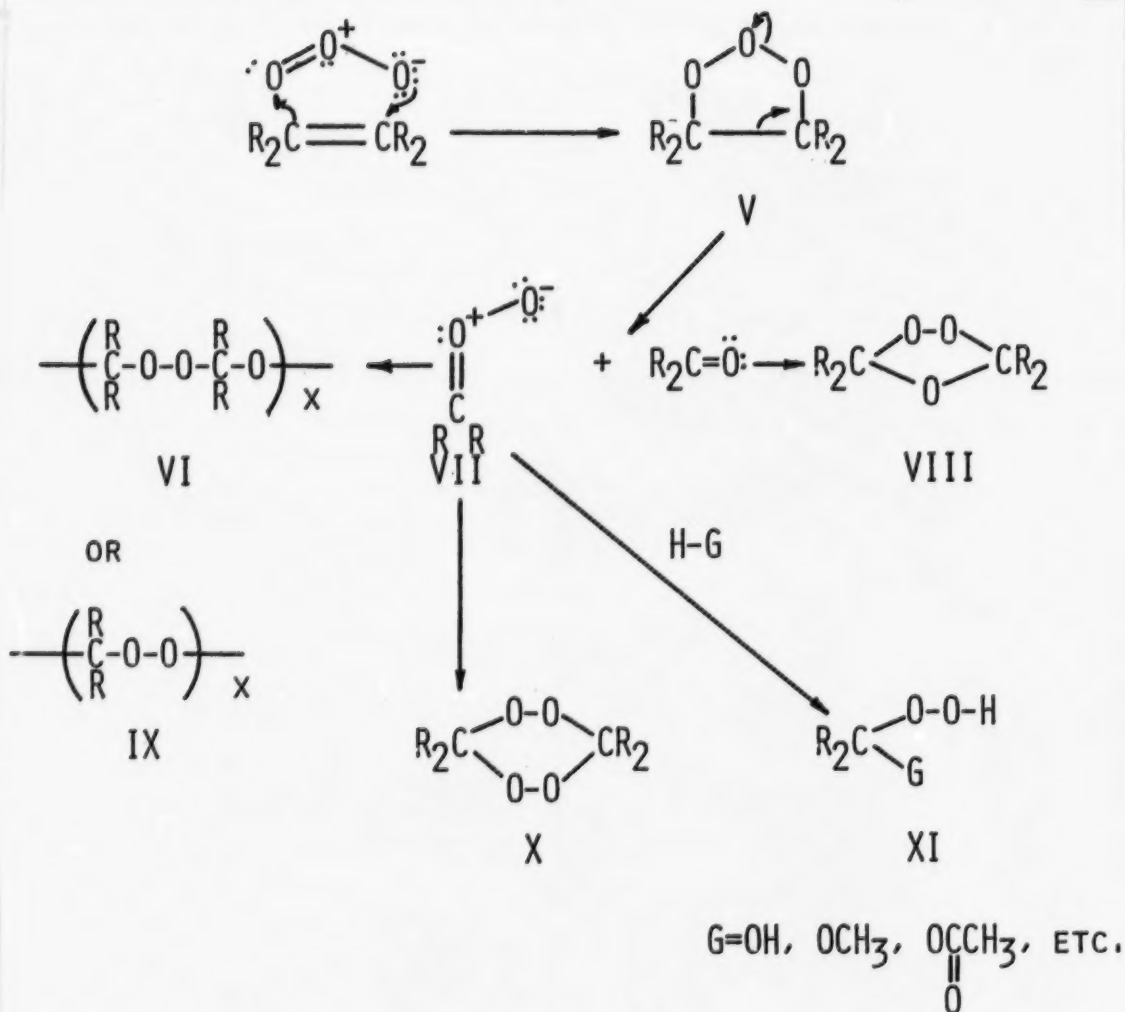


Figure 16. Crigee modified ozonolysis reaction pathways.

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ring destroyed to form formic and acetic acids.

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The reaction of ozone with aldehydes, ketones, alcohols, and ethers is an ozone initiated reaction. Ozone acts as the initiator after which oxygen enters into the reaction. In general, reactions proceed slowly at ambient temperatures and not at all if more reactive species are present. Mechanisms of reaction are somewhat in question, but probably begin with an ozone attack on the carbon chain followed with auto-oxidation by molecular oxygen.

Organic compounds containing a nucleophilic atom in their structure such as sulfides, phosphites, and amines are readily attacked by ozone. Sulfides are oxidized first to sulfoxides and eventually to sulfones. Phosphites are easily converted to phosphates. Ozonation of primary and secondary amines leads to the formation of nitro compounds and nitroxides, all from an electrophilic attack by ozone (28).

OZONATION SPECIFIC METHODS AND MATERIALS

Ozonation System — 6-1/2" —

The ozone used was generated by a Grace Model LG-2-L2 (Davison Chemical Company) corona ozone generator using bottled dry oxygen as the gas source. Oxygen was first dried and filtered through a TekLab FD-0235 transparent filter/drier then directed to the ozone generator via Eastman three-eighths inch Polyflo polyethylene tubing. The ozonator was operated at a pressure of 86.2 kPa, an oxygen flowrate of 10 scfh, and a variable power setting of 0 to 300 watts. The calibration curve for ozone generated at various power settings is shown in Figure 17.

Ozone was directed to the reactor through polyethylene tubing, where it entered the bottom of the column. A porous stone diffuser was used for initial ozone dispersion. To aid in gas transfer, 6.3 mm ceramic Raschig rings were placed in the column to a depth of 1.52 m. The reactor consisted of two 1.52 m sections of 5.08 cm diameter pyrex glass tubing with an expansion globe located at the top which served as an aid in breaking foam generated during the experiments. A schematic diagram of the system is given in Figure 18.

The test wastewater samples were removed from the bottom of the column through a glass recirculation line and returned to a spray nozzle located in the expansion globe. Glass tubing was used wherever possible to minimize the potential for desorption of phthalates during the ozonation studies. Cole-Parmer 6408-09 tygon tubing was used only for making connections between the various sections of glass tubing. The wastewater was recirculated at a rate of four liters per minute by a number 7018 Masterflex peristaltic pump head attached to a Cole-Parmer 3200 rpm motor.

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The off-gas from the reactor was directed via three-eighths inch Eastman polyflo tubing to two 500 milliliter gas washing bottles arranged in series for ozone analysis. Three sets of gas washing bottles were arranged in parallel. Two sets contained a solution of buffered potassium iodide while the

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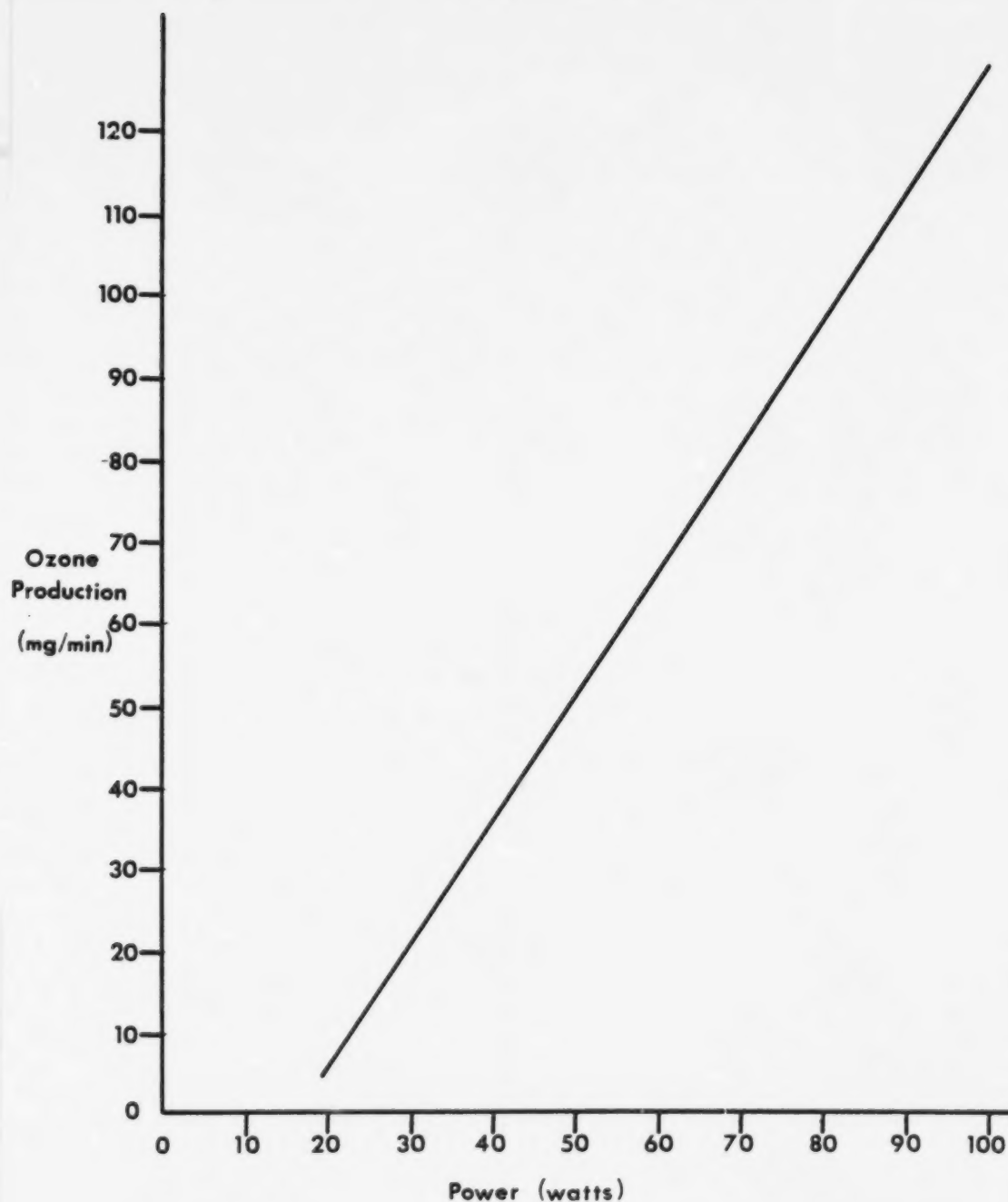


Figure 17. Ozone calibration curve for LG-2-L2 corona generator.

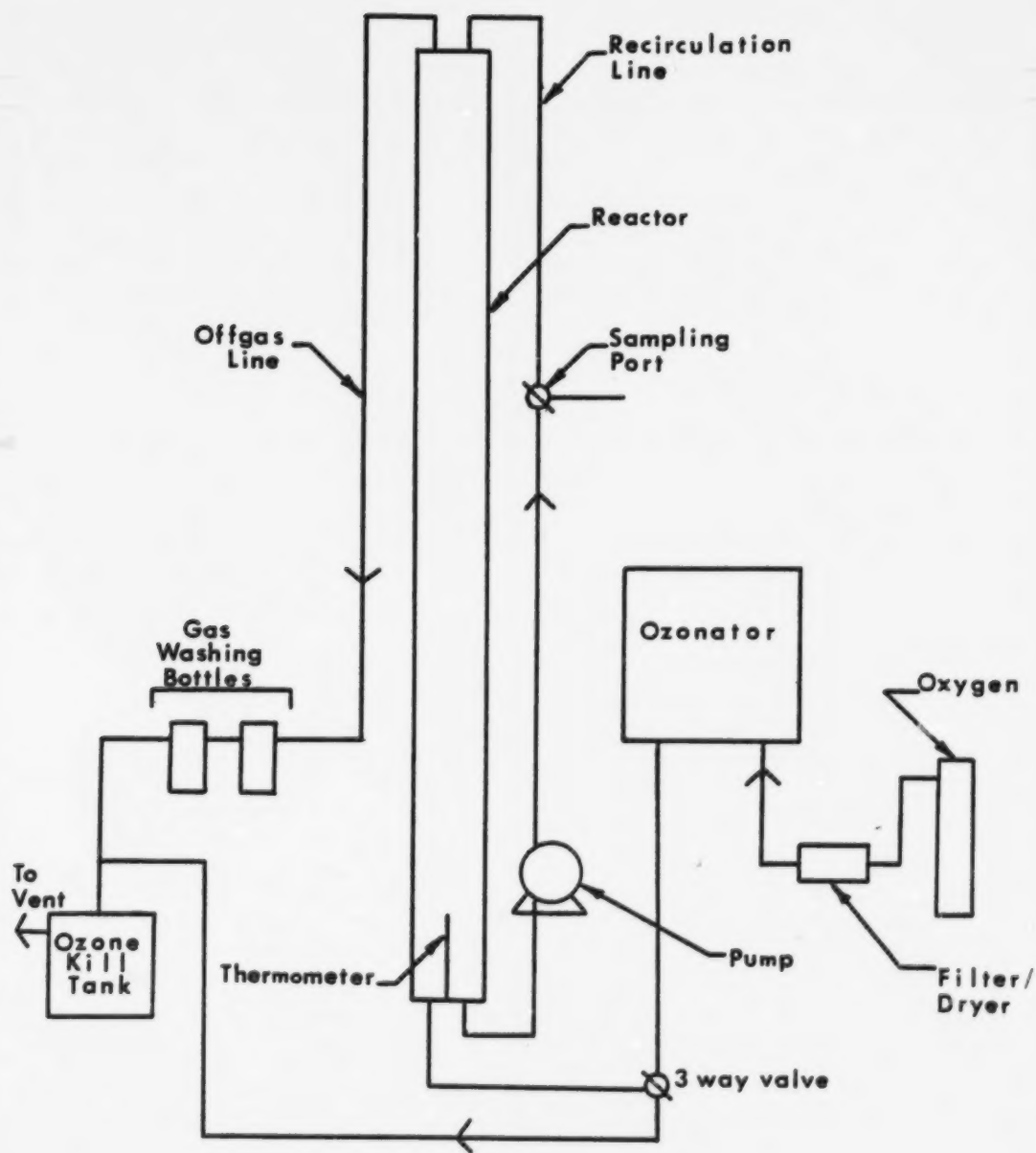


Figure 18. Schematic drawing of laboratory-scale ozonation system.

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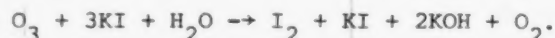
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third contained distilled water to detect gas flow. Any unreacted ozone that passed through the gas washing bottles was vented to a 20 liter tank containing a saturated solution of sodium thiosulfate. The exhaust from the 20 liter tank was discharged to the atmosphere.

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Analytical Techniques

Ozone off-gas measurements were made using a modification of methods described in Standard Methods for the Examination of Water and Wastewater (7) and Methods of Air Sampling and Analysis (34). The method is based on liberation of free iodine when ozone is absorbed in a solution of potassium iodide according to the stoichiometric equation



Previous work has shown that iodine liberation is pH dependent when ozone is added to iodide solutions. Boyd *et al.* (35) and Dietz *et al.* (36) have shown that more iodine is liberated in acidic than in basic solutions. Because the stoichiometry of the ozone-iodide reaction (36,37) has been proven to be 1:1 at pH 7, a solution of 2 percent potassium iodide solution was buffered using 0.1M potassium dihydrogen phosphate to a pH of 7.0. The solution was stored in brown glass bottles to prevent photodegradation during storage. At the time of sampling, reactor off-gas was bubbled through two 500 milliliter aliquots of buffered potassium iodide for a measured time interval. Liberated iodine was then titrated with 0.25N sodium thiosulfate solution using starch indicator. The sodium thiosulfate solution was standardized daily using 0.25N potassium dichromate as the primary standard.

RESULTS OF OZONATION STUDIES

Three types of ozonation studies were conducted. The first consisted of a preliminary ozonation characterization study designed to define the experimental conditions required for the conduct of the priority pollutant oxidation study. The second focused on defining the influence of pH and temperature on the kinetics of ozonation of dyestuff manufacture wastewaters while the third consisted of the priority pollutant oxidation study itself.

Preliminary Studies

The preliminary ozonation characterization studies were directed toward evaluating the degradation of color, organics, pH changes and ozone consumption levels. Experimental samples were collected from the influent to the wastewater treatment facilities of the six participating dyestuff manufacturers and were ozonated batchwise to an ozone application level of three grams ozone per gram of COD initially present. This application level was selected on the basis of a study conducted by Palmer (38). Moreover, all preliminary studies were conducted at a temperature of 20°C and all wastewaters were neutralized to a pH of 7.0 prior to ozonation with the exception of wastewater sample A which had been collected after neutralization. The pH of this neutralized wastewater was 7.7.

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Color Reduction--

During the course of ozonation, visible spectral shifts occurred for all six dyestuff manufacture wastewater samples studied. The shifts are shown in Figures 19 and C1 to C5 for the manufacturers' wastewaters coded A through F, respectively. Generally, these shifts agree with the observations of Bailey (30) who found that organic color compounds are very amenable to oxidation by ozone.

Color in organic molecules is associated with highly conjugated double bonds. Such double bonds absorb parts of the visible spectrum and reflect others due to their electronic make-up. The apparent color of the organic molecule is identified by the reflected light. When dyestuff molecules are treated with ozone, the reaction ensues at the conjugated bonds. The overall effect is to shift the absorption maximum out of the visible spectrum.

For the present studies the maximum absorbance occurred near the low end of the visible span for all but the B and F samples. As expected, these were visually of a yellow-brown color while the B sample had a deep red color and the F sample a blue-green color. Upon ozonation, all spectra shifted into the ultraviolet region. Complete elimination of the visible spectra was not achieved, even with an ozone application level of three grams per gram of COD initially present.

Degradation of the color value for each of the samples was rapid as a result of ozonation, Figures 20 and C6 to C10. Essentially complete color removal was observed for the B and F samples for ozone application levels of 1.76 and 2.25 g O₃/g initial COD. The remaining dyestuff manufacture wastewater samples (A, C, D, & E) proved somewhat more resistant to complete color value removal. Nonetheless, color value removals ranged from 88 to in excess of 95 percent for these samples at an ozone application level of 3 g O₃/g initial COD. A baseline color value of 0 to 300 ADMI units was attained in all cases. Similar results are documented by Netzer *et al.* (39) who achieved excellent color removals using ozone for treating wastewaters obtained from carpet, hat, and yarn dyeing houses.

Total Organic Carbon Removals--

TOC removal can occur through two pathways: (i) oxidation of organic materials to carbon dioxide, which is subsequently purged from the reactor, or (ii) generation of volatile organics from nonvolatile precursors that are subsequently also purged as shown by Sievers, *et al.* (40). During these preliminary studies TOC removals ranged from 15 to 42 percent at an ozone application level of 3 O₃/g COD initially present at which point each experiment was terminated. The time dependent traces for these oxidation studies conducted on samples A through F are shown in Figures 21 and C11 to C15, respectively.

Ozone consumption Rates--

The mass of ozone that passed through the reaction column increased during all preliminary experimental studies. Time traces of ozone consumption rate are presented in Figures 22 and C16 to C20 for samples A through F, respectively. The initial ozone consumption rate expressed as percentage of the ozone application rate ranged between 90 and 100 percent for all samples.

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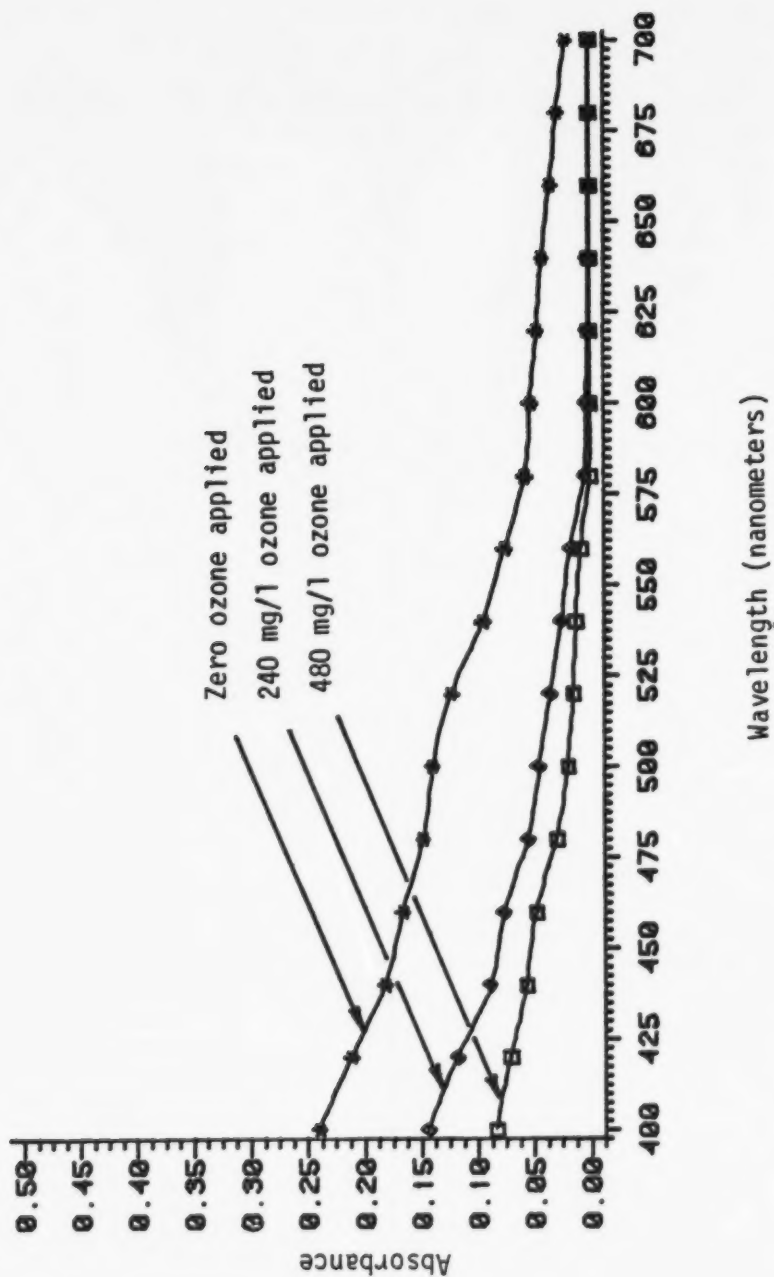


Figure 19. Visible spectral shifts due to ozonation for sample A.

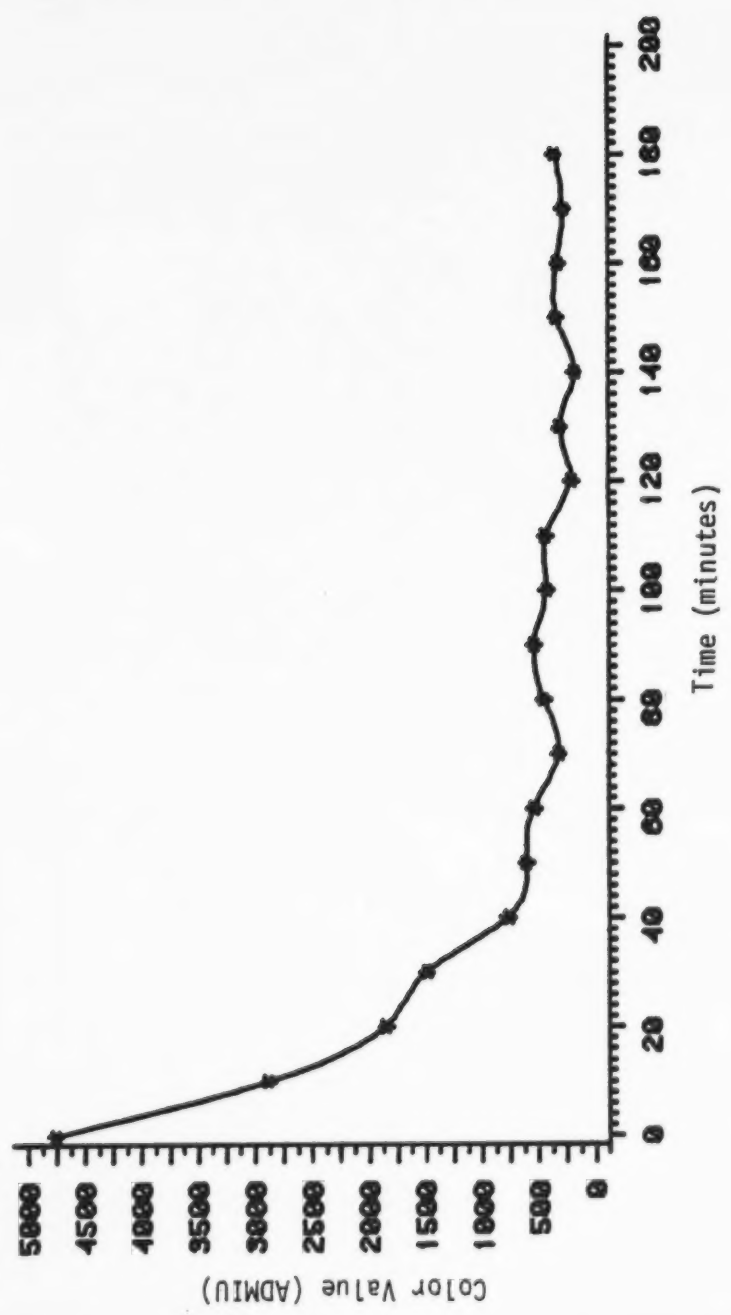


Figure 25. Color value degradation due to ozonolysis for sample A.

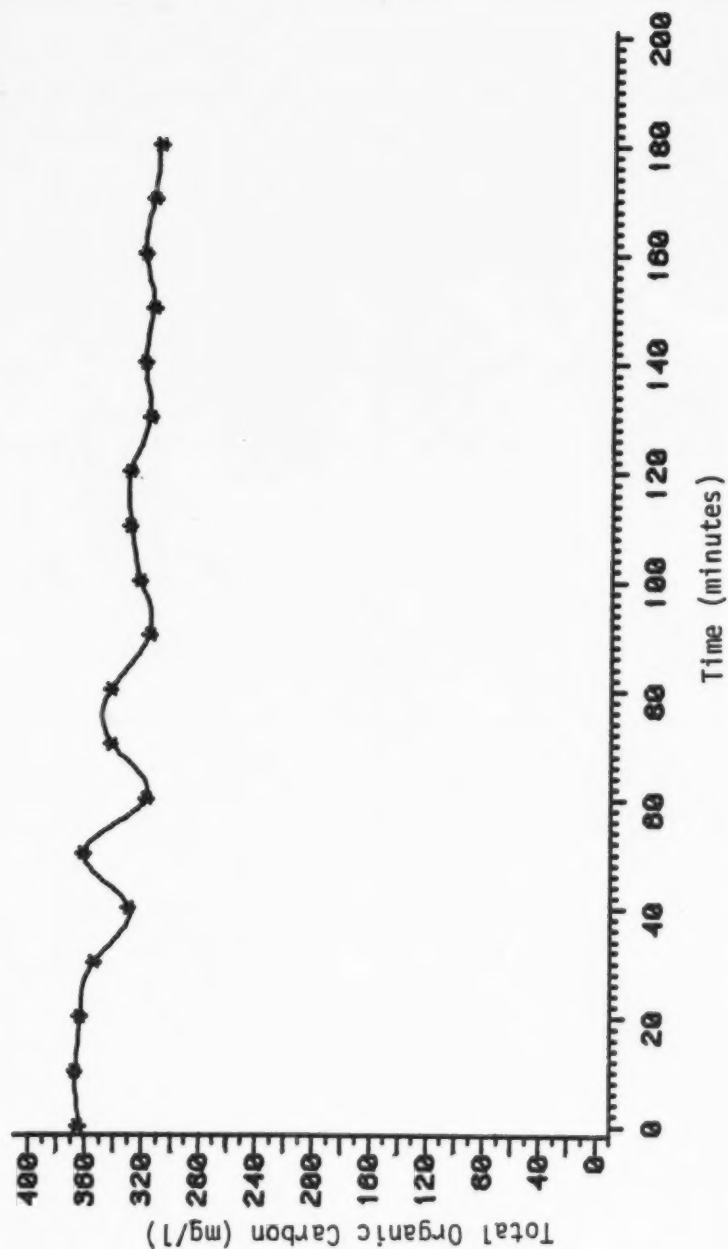


Figure 31. TOC degradation due to ozonolysis for sample A.

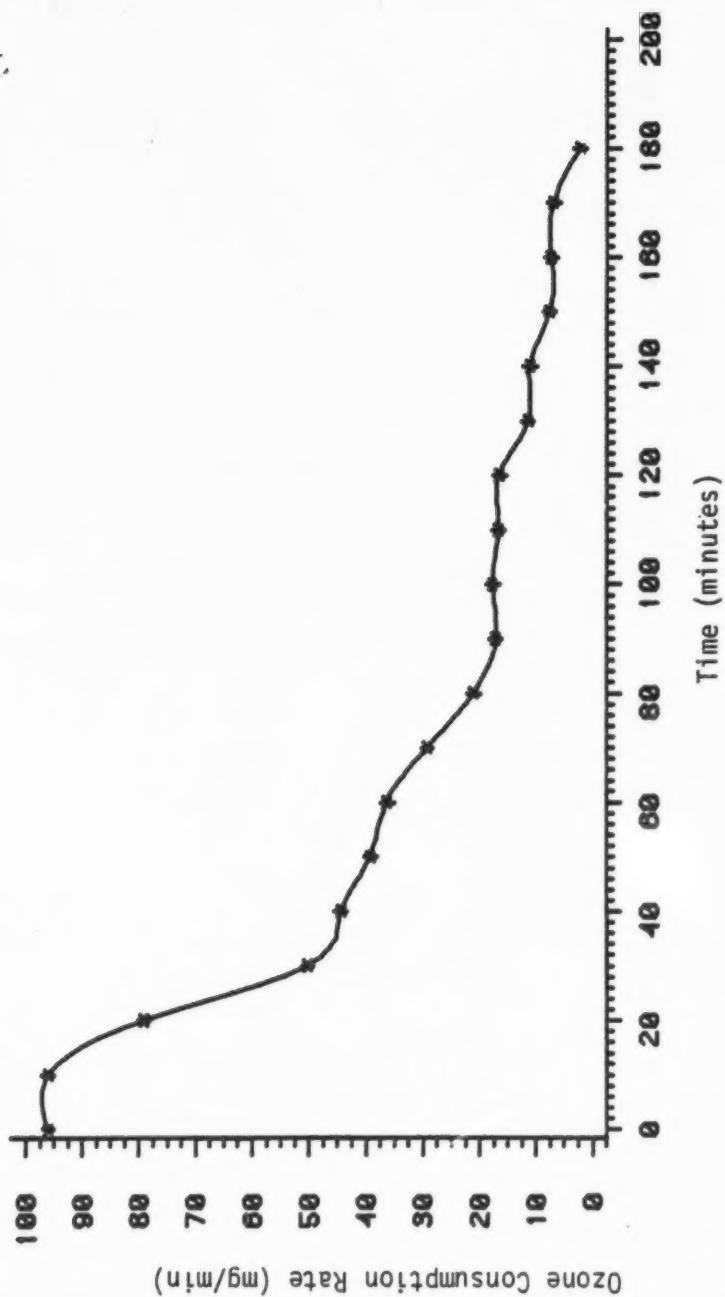


Figure 37. Ozone consumption rate for sample A.

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At the termination of each study, consumption rates were approximately 2 to 10 percent of the ozone application rates with the exception of sample F for which the final ozone consumption rate was equal to approximately 40 percent of the application rate. The consumption rate curves paralleled rather closely the time traces of color value degradation with the exception of sample F.

O₃/TOC Utilization Ratio--

The ratio of ozone utilized per unit of TOC removed versus time traces are presented in Figures 23 and C21 to C25 for the A through F dyestuff manufacture wastewater samples. Generally, the O₃/TOC utilization ratios did not change appreciably throughout these preliminary experiments although a slight increase in the ratio was observed for several of the studies as they progressed. The highest O₃/TOC ratios, 20 to 30 g O₃/g TOC, were observed for the A, C, and D samples which proved to be most refractory in character. The B and F samples were observed to have comparatively low ozone utilization ratios, in the range of 7 to 10 g O₃/g TOC oxidized, while the E sample was observed to have an intermediate ozone utilization ratio. The relative ratios provide an indication of the comparative refractory nature of these dyestuff manufacture wastewaters, but do not provide an absolute index relative to the ozonation of other materials.

Refractory Index--

A quantitative scale, previously established by Prengle and Mauk (41), is termed the refractory index (RFI) which is an index of the difficulty of oxidation by ozone. The refractory index was defined as

$$RFI = B^{\circ} t_{1/2} / A_o$$

where

RFI = refractory index (hrs),

B[°] = ozone applied to reduce concentration to half the initial (g),

t_{1/2} = time for one-half conversion of A_o (hrs),

A_o = initial amount of compound (g).

The RFI can also be applied to the ozonation of dyestuff manufacture wastewaters; in this case based both on TOC or color value degradation. The RFI values for the dyestuff manufacture wastewater samples evaluated are presented in Table 28 using both TOC and color value as indices. To illustrate the refractory nature of these wastewaters as compared to other compounds, a listing of refractory indices for other compounds is also presented. The refractory indices are qualitatively described as slightly refractory (RFI<1), refractory ((RFI>100), highly refractory (RFI100>1000), and very highly refractory (RFI>1000).

All calculated refractory indices based on color value degradation can be categorized as slightly refractory for these samples. On the basis of TOC, however, the calculated RFIs fell into the refractory and highly refractory ranges. This illustrates the reactive characteristics of the dyestuff manufacture wastewaters in comparison to other compounds.

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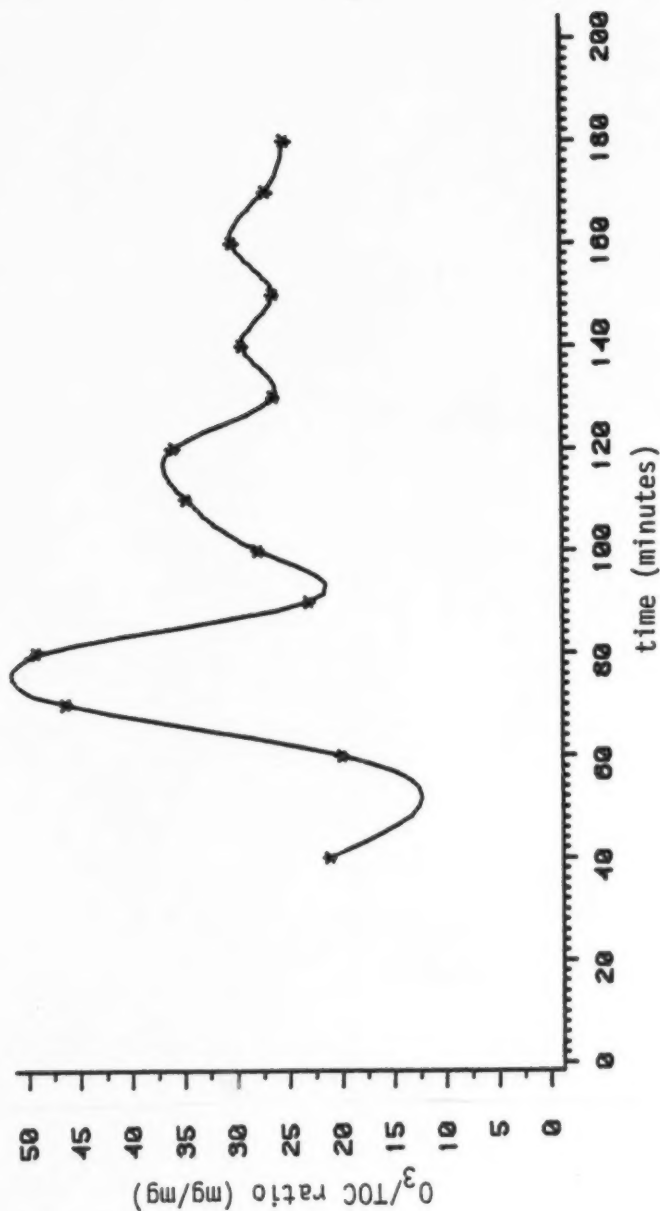


Figure 43. Time dependence of O₃/TOC ratio for sample A.

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TABLE 28. REFRACTORY INDICES FOR DYESTUFF MANUFACTURE WASTEWATERS AND OTHER COMPOUNDS (after Prengle and Mauk, 41)

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Compound	RFI (hours)	Qualitative Scale
*Sample B	0.0029	Slightly Refractory
*Sample C	0.0094	
*Sample F	0.021	
*Sample E	0.038	
*Sample D	0.069	
*Sample A	0.080	
Potassium Cyanide (KCN)	0.41	
Phenol	0.44	
Chloroform	0.55	Refractory
Pentachlorophenol	1.6	
Glycine	19.7	
Palmitic Acid	27.3	
Nitrosodimethylamine	31	
Baygon	37	
#Sample B	48	
#Sample D	51	
Dichlorobutane	56	Highly Refractory
Methanol	88	
Vapam	102	
#Sample F	110	
Glycerol	112	
o-Dichlorobenzene	110	
#Sample E	163	
Polychlorinated Biphenyls	200 (est.)	Very Highly Refractory
Ethanol	250	
#Sample C	246	
Complexed Ferricyanide	270	
DDT	297	
#Sample A	400	
Acetic Acid	>1000	
Malathion	>1000	

Notes: *RFI based on color value degradation
#RFI based on TOC degradation

pH Changes--

As mentioned previously, all dyestuff manufacture wastewaters were neutralized prior to ozonation to a pH of 7 with the exception of sample A. Upon initiating ozonation, the pH shifted rapidly to a new value towards the pH of the wastewater prior to neutralization as is shown in Figures 24 and C26 to C30. After this initial shift, additional changes in pH were small and generally toward neutrality. These changes are in agreement with data

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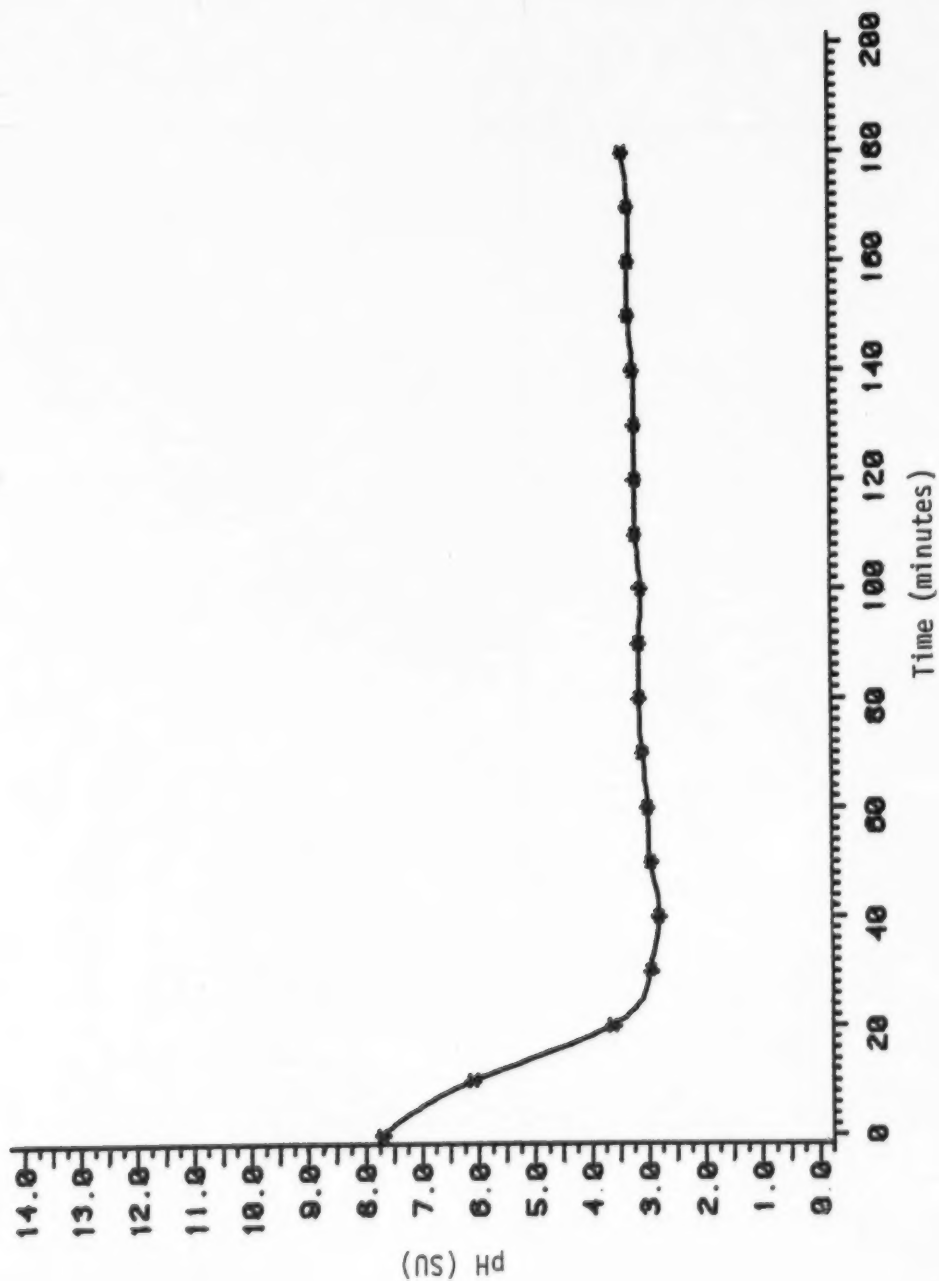


Figure 49. Time dependence of pH for ozonation of sample A.

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presented by Evans (22) who conducted ozonation studies on wastewaters and observed pH changes in the direction of neutrality. On the basis of these results it appears that organic intermediates that contained acidic or basic functional groups were rapidly formed as a result of ozonation. The residual intermediates appear to be relatively refractory in character.

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Rates of Degradation

Because treatability studies (24,31,32,33,37) have shown increased oxidation rates at high pH values due to the increased presence of hydroxyl radicals, a kinetics study was initiated to ascertain the effects of various initial pH and temperature values on the rates of degradation of TOC and color in dyestuff manufacture wastewaters. Statistical inference was used to obtain estimates of degradation rates and their associated confidence levels.

Kinetic experiments were conducted at temperatures varying from 10 to 24°C and pH values ranging from 3 to 7. Kinetic studies were conducted for five of the six wastewater samples. Sample D was omitted from this study. The various experimental levels used during this investigation are given in Table 29. Since reaction rates are influenced by temperature according to the Arrhenius relationship, inverse temperature was used in selecting experimental levels for the kinetics study. Accordingly, experimental temperatures of 10, 13.3, and 20°C and 12, 16, and 24°C were used since they provided approximately equal spacing of inverse temperature.

Duplicate runs were performed to obtain an estimate of the error variance associated with sampling and analysis. All rates were pooled to gain a better estimate of the variance and the statistical t-test was used to determine the 95 percent confidence intervals. All data points were used when determining the TOC degradation rate using the method of least squares. The first order region which consisted of the first three data points was used when determining the color value degradation rate.

TABLE 29. EXPERIMENTAL LEVELS UTILIZED IN OZONATION KINETICS STUDY

Sample	pH	Temperature °C
A,B	3	10
A,B	3	20
A,B	5	13.3
A,B	7	10
A,B	7	20
C,E	3	12
C,E	3	24
C,E	5	16
C,E	7	12
C,E	7	24
F	7	10
F	7	20
F	9	13.3
F	11	10
F	11	20

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Results of the various rate studies are presented in Table 30 for the rate of TOC degradation and in Table 31 for color value degradation for samples A, B, C, E, and F, respectively. Statistical comparison of the rates for TOC and color value degradation showed that all calculated rates fell within the 95 percent confidence interval, with one exception. Only the TOC degradation rate for sample F at pH 11 and a temperature of 20°C was found to be statistically significantly higher than those calculated from other experiments. This implies that no statistically significant differences exist between the rates of degradation at different system temperatures and pH's. Accordingly, one would not expect that significant benefits could be derived relative to oxidation rates through pH or temperature control. One may also conclude that oxidation rates are relatively insensitive to changes in pH and seasonal temperature variations.

An analysis of reaction order was also undertaken for both TOC and color value degradation. Reaction orders investigated were zero, first, and second. At the 95 percent confidence level, reaction order could not be discerned since all three were determined to be applicable for description of the TOC degradation rate data. Color value degradation data fit both the first and second order rate relationships, but not the zero order relation.

A qualitative comparative study between experimental extremes was also investigated for the measured parameters. No significant changes in ozone consumption, pH value shifts, or O_3 /TOC ratio were found. As a result, significant changes in the treatment of each of the dyestuff manufacture wastewaters using ozone would not be expected.

Organic Priority Pollutant Removal Studies

To establish the technical feasibility of using ozonation for removing organic priority pollutants from dyestuff manufacture wastewaters, a treatability study was conducted on each of the six wastewaters. These were conducted batchwise at ozone application levels determined on the basis of the preliminary studies.

Initially, three criteria were defined for determining the appropriate ozone application levels. These were: (i) mass of ozone utilized per unit mass of total organic carbon oxidized, (ii) TOC degradation, and (iii) color value degradation. Because the time dependent traces of TOC degradation and the ratio of O_3 utilized/TOC oxidized showed no significant discontinuities that could serve as the basis for establishing ozone application levels, the time trace of color value degradation was selected for establishing ozone application levels for all organic priority pollutant ozonation studies.

As noted previously, degradation of the color value could be described by a first-order kinetic relationship. For this reaction order, the associated time constant of the system is equal to the time required to attain 63 percent color value removal in a batch system. To attain removals of approximately ninety-five percent in a continuous-flow, plug-flow reactor operating at steady state, the design hydraulic residence time for the system would have to equal a minimum of three time constants. Accordingly, these ozonation studies were conducted batchwise on 4 liter samples for a period of time that equalled

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TABLE 30. TOC DEGRADATION RATES FOR KINETICS STUDY

Sample	Temperature (°C)	Initial pH (SU)		
		3	5	7
A	10	0.25		0.33
	13.3		0.32	
	20	0.34		0.35
B	10	0.29		0.30
	13.3		0.42	
	20	0.31		0.39
C	12	0.45		0.40
	16		0.38	
	24	0.37		0.39
E	12	0.34		0.55
	16		0.57	
	24	0.52		0.55
F	10	1.01		1.07
	13.3		1.04	
	20	1.08		1.55

Note: Rates are averages of duplicate runs and are given in milligrams TOC/l-min.

TABLE 31. COLOR VALUE DEGRADATION RATES FOR KINETICS STUDY

Sample	Temperature (°C)	Initial pH (SU)		
		3	5	7
A	10	0.01223		0.01221
	13.3		0.01347	
	20	0.01352		0.01319
B	10	0.02539		0.02743
	13.3		0.02995	
	20	0.02874		0.03204
C	12	0.04838		0.04834
	16		0.04893	
	24	0.04539		0.04638
E	12	0.01998		0.01990
	16		0.01987	
	24	0.01755		0.01709
F	10	0.02942		0.03246
	13.3		0.03193	
	20	0.02892		0.03001

Note: Rates are averages of duplicate runs and are given in log color value/min.

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three characteristic time constants for the system at ozone application rates that were identical to those used in the preliminary studies. The time constants, required ozonation times, associated ozone application rates and levels, and initial and residual color values are given in Table 32 for each of the five wastewater samples investigated.

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TABLE 32. OZONATION PARAMETERS FOR PRIORITY POLLUTANT STUDY

Parameter	Sample					
	A	B	C	D	E	F
Time Constant (min)	23.1	13.0	8.6	21.8	15.4	15.9
Treatment Time Required (min)	69.4	39.0	25.8	65.4	46.2	47.8
Ozone Application Rate (mg/min)	96	51	125	96	102	126
Ozone Applied (mg/l)	1665	500	806	1570	1178	2000
Initial Color Value (ADMIU)	4579	19290	6949	1957	4985	17978
Residual Color Value (ADMIU)	480	1000	605	170	1395	1000

Note: Sample volume was 4 liters.

The results of these ozonation studies are given in Table 33 for the dyestuff manufacture wastewater samples coded A through D and F, respectively. It is to be noted that no analyses for volatile organic priority pollutants were conducted due to the fact that previous studies have shown that such materials are generally completely stripped and/or oxidized in ozonation systems. The analytical program for this study, accordingly, focused entirely on the acid and base neutral extractable priority pollutant fractions.

Results for the A and B samples showed that all of the priority pollutants initially present in these wastewater samples were removed to levels below detectability. It is important to note, furthermore, that no organic priority pollutants were produced as a result of ozonation. For sample C, both bis (2-chloroethyl)ether and N-Nitrosodiphenylamine were removed to non-detectable levels. Nonetheless, phenol which was initially present at a concentration level of 1900 micrograms per liter was reduced to an average concentration of 12 micrograms per liter representing a removal level in excess of 99 percent.

The situation for samples D and F was somewhat different, however. In the case of sample D, four of the organic priority pollutants initially present were removed to less-than-detectable levels. Phenol was present in the ozonated sample at an average concentration of 15.5 micrograms per liter representing a removal efficiency of approximately 93 percent. In contrast, the concentration of nitrobenzene which was initially 830 micrograms per

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TABLE 33. ACID AND BASE/NEUTRAL FRACTION OF PRIORITY POLLUTANTS PRIOR TO AND AFTER OZONATION

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Sample	Compound	Concentration (µg/l)			
		Initial		Final	
		Dup #1	Dup #2	Dup #1	Dup #2
A	2-Nitrophenol	40	35	*ND	ND
	Phenol	110	120	ND	ND
	2,4-Dinitrophenol	350	340	ND	ND
	1,4-Dichlorobenzene	3.4	3.1	ND	ND
	Naphthalene	1.6	1.4	ND	ND
B	2,4-Dichlorophenol	1.3	1.3	ND	ND
	2,4-Dinitrophenol	3200	3300	ND	ND
	1,4-Dichlorobenzene	50	6.2	ND	ND
	Nitrobenzene	51	47	ND	ND
	Di-n-butylphthalate	22	24	ND	ND
C	Phenol	1900	# -	13	11
	Bis (2-Chloroethyl)ether	2300	-	ND	ND
	N-Nitrosodiphenylamine	29	-	ND	ND
D	1,3-Dichlorobenzene	1.0	-	ND	ND
	Phenol	240	-	15	16
	1,4-Dichlorobenzene	9.4	-	ND	ND
	Naphthalene	16	-	ND	ND
	1,2,3-Trichlorobenzene	8.5	-	ND	ND
	Nitrobenzene	830	-	360	400
F	Phenol	59	57	26	32
	Di-n-octylphthalate	1800	1800	360	350

* ND means not detected.

Duplicate samples were not run.

liter was decreased to only 380 micrograms per liter (54 percent removal). The two organic priority pollutants present in sample F proved to be even more resistant to degradation by ozonation. For this sample, residual levels of phenol of 29 micrograms per liter and of Di-n-octylphthalate of 355 micrograms per liter were observed after ozonation. This represents treatment levels of 50 and 80 percent, respectively.

The lower treatment level observed for the F sample is likely attributable to the fact that the concentration of organic materials expressed as TOC was approximately three times the magnitude of the TOC in the other four samples. The comparatively higher concentrations of competing compounds would tend to inhibit the rate of degradation of specific organic compounds by ozone, thereby resulting in lower removal efficiencies at specific ozone application levels.

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In the case of samples C, D, and F, higher ozone application levels than were used in this study would be required to attain higher removal levels in prototype systems. Conversely, lower ozone application levels could potentially give effective treatment levels for samples A and B. Kinetic studies on priority pollutant degradation would have to be conducted on any specific wastewater before an effective ozone application level could be selected.

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REACTOR SIZING AND ASSOCIATED COSTS

Reactor Sizing

Reactor design was based on kinetic data obtained from color value removal and ozone consumption rates for the six dyestuff manufacture wastewaters. The objective of the design is to obtain the residual color values given in Table 34. These correspond with color values obtained at the ozone application levels selected for priority pollutant removal studies. It is assumed, therefore, that such designs will also provide for effective organic priority pollutant removals.

TABLE 34. PROJECTED VOLUME REQUIREMENTS FOR REACTORS

Dyestuff Manufacture Wastewater	Effluent Color Value (ADMIU)	Volume Required (m ³)		Ozone Production Requirements (kg/day)
		CSTR	CSTR Cascade	
A	480	13700	1600	25600
B	1000	1426	417	4630
C	605	5200	355	11280
D	170	3160	662	8450
E	1390	1530	439	9470
F	1000	1680	529	19620

Color value degradation rates were defined as the slope of the color-time traces at the corresponding color value. Rates of color value degradation are shown as a function of color value in Figure 25 for sample F. It should be noted that the rate of color value removal is much more sensitive to color value at low color values. This results in significant increases in required reactor volume if low residual color values are desired. The design procedure for wastewater sample F is presented herein as the analog used for all dyestuff manufacture wastewaters.

The first step in reactor design is to develop a relationship between color value removal and ozone consumption rates. If the ozone-color reaction is represented by a stoichiometric equation, then the rate of ozone consumed is proportional to the rate of color value removal as shown in Figure 26. Melynk, et al. (42) have also shown this to be the case for pulp bleachery wastewaters. The proportionality constant is estimated from the slope, using

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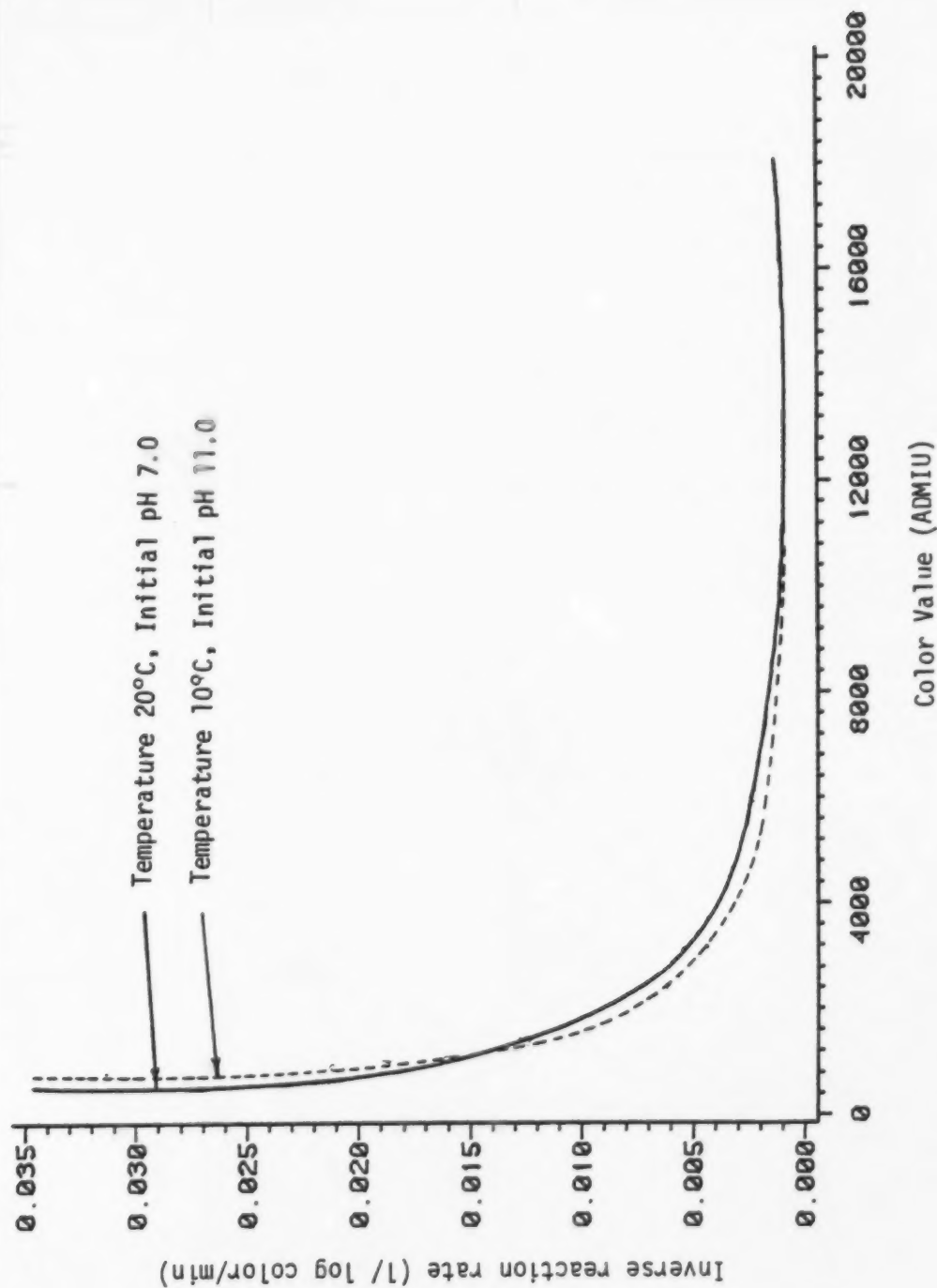


Figure 55. Inverse reaction rate as a function of color value for sample F.

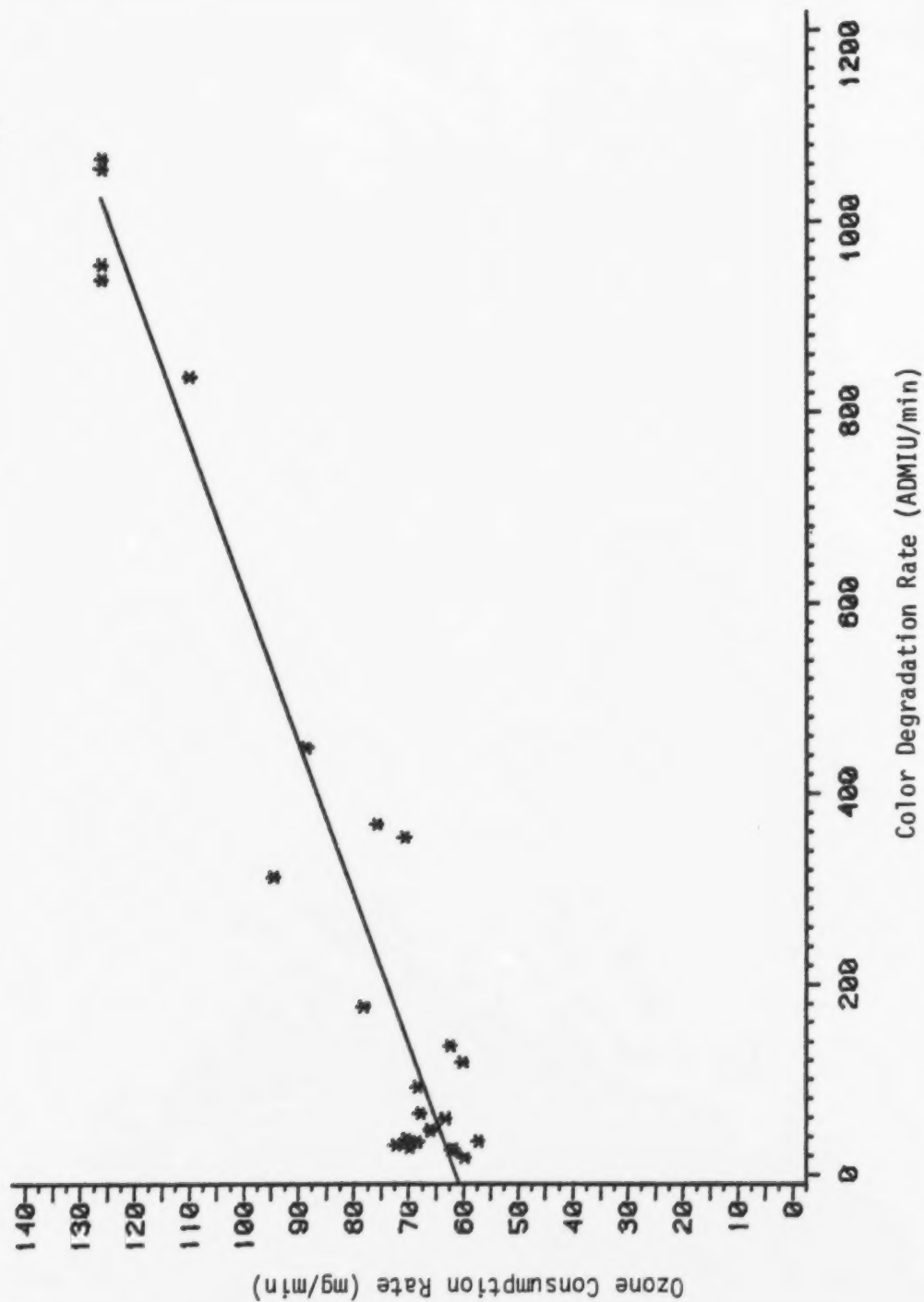


Figure 56. Ozone consumption rate as a function of color removal rate for sample F.

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the method of least squares. A positive intercept indicates that an ozone demand from an unidentified chemical reaction occurred simultaneously with the ozone-color reaction. The relationship between ozone consumption and color value removal rates eventually lead to the ozone production requirements required for treatment.

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To size the required volumes for the reactor, the area under the curve given in Figure 27 between abscissa values that correspond to the influent and effluent color represents the residence time required for treatment. This assumes that one utilizes an idealized plug-flow tubular (PFTR) reactor. Conversely, if one assumes the hydraulic regime to be a completely mixed, continuous-stirred tank reactor (CSTR), the required residence time is equal to the rectangular area defined by the influent and effluent color values and corresponding inverse reaction rate. Because the color value in the reactor contents equals the effluent value, the appropriate inverse color value degradation rate is equal to that of the effluent.

To approximate the hydraulic regime usually encountered in ozonation columns, a cascade of three idealized CSTR's was used. It should be noted that this flow regime was used to determine the required reactor volume and to develop the corresponding costs. The reactor residence time can be optimized by using a graphical procedure developed by Levenspiel (43). The procedure is illustrated by the example shown in Figure 27. Vertical lines constructed from the upper corners of the shaded areas define rectangular areas whose residence time is equal to the residence time of the reactors. Minimizing these areas and thus the required residence time is accomplished when the tangent to the inverse rate curve is parallel to the diagonal which connects the upper right-hand corners of two adjacent triangles. The sum of the residence times equals the residence time of the reactor. Selection of these tangents is accomplished by trial and error.

For purposes of design, a target flowrate of 11,340 m³/d was assumed. This is typical of wastewater treatment plants found in the dyestuff manufacturing industry. Required reactor volumes for the six dyestuff manufacture wastewaters are given in Table 34 both for a CSTR and a CSTR cascade. Ozone production requirements were estimated by calculating the ozone consumption rate experienced in each CSTR, then summing each requirement. By knowing the color value degradation rate from Figure 25. The ozone consumption rate is then found using the relationship given in Figure 26.

Projected Treatment Costs

Capital cost estimates were prepared for an installed ozonation system, including ozone generators, dissolution equipment, gas preparation, instrumentation, valving, oxygen generation, and other engineering design and assistance costs. Capital costs of ozonation systems demonstrate significant economics of scale. For this size plant, a cost of \$1300 per kg-ozone/day of installed production capacity was assumed. Capital costs are amortized at 12 percent for 20 years. Both capital and operating costs were taken from Katz (44).

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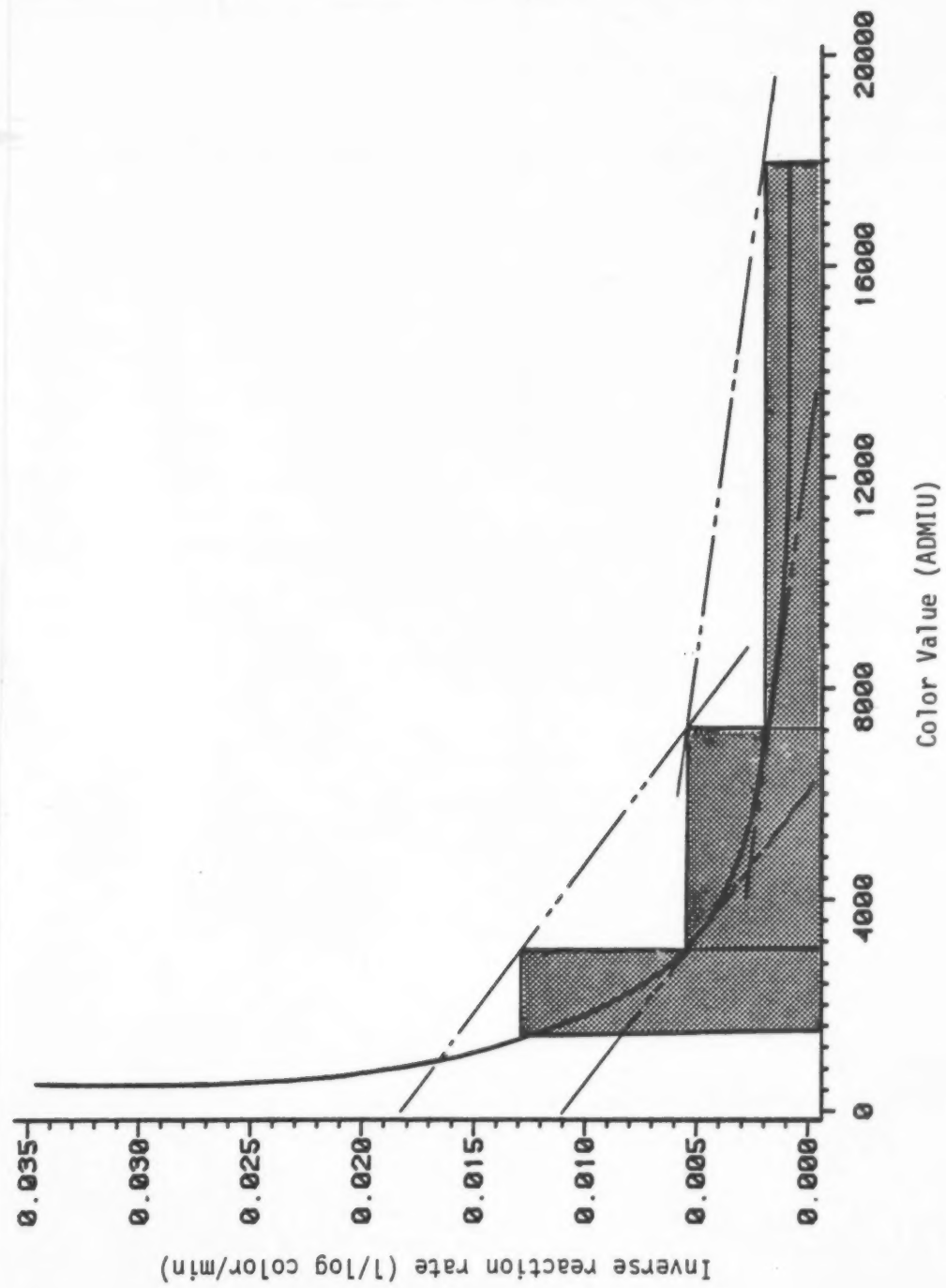


Figure 57. Maximization of rectangles technique for determining reactor residence time.

Operating costs for ozonation depend to a large degree upon the cost of electricity. Assuming a cost of 4 cents/kilowatt hour, and an energy consumption level of 20 watt hours/gram of ozone produced, operating costs were estimated. These costs include estimates for electrical consumption for ozone production, injection, oxygen production, and ancillaries. The total cost estimates are given in Table 35.

TABLE 35. COST ESTIMATES FOR ORGANIC PRIORITY POLLUTANT REMOVAL BY OZONATION

Dyestuff Manufacture Wastewater	Operating Cost (\$/1000 m ³)	Capital Cost (\$/1000 m ³)	Total Cost (\$/1000 m ³)
A	1810	1100	2920
B	330	200	530
C	800	490	1280
D	600	360	960
E	670	410	1030
F	1390	840	2230

These costs represent values which are extremely high for two of the five dyestuff manufacture wastewaters. Four of the dyestuff manufacture wastewaters compared favorably in cost to the system proposed by Arisman (45) for PCB removal. The high cost is due to two factors; high ozone demands and high degrees of treatment required to attain the presumed level of color and priority pollutant removal.

SUMMARY

Ozonation studies conducted on six dyestuff manufacture wastewaters showed the following relative to performance: (i) low to moderate reductions in organic carbon (as indexed by TOC) were obtained; (ii) excellent color value removals were achieved (87 to 100 percent) with ozone application levels ranging from 460 to 2900 g/m³, (iii) although many organic priority pollutants were removed to levels below detectability some proved to be comparatively resistant to oxidation by ozone; and (iv) no priority pollutants were produced as a result of ozonation. It was shown, furthermore, that neither pH nor temperature exerted statistically significant effects on ozonation kinetics for the experimental range investigated. Costs for an ozonation system designed to provide effective removals of priority pollutants were projected at \$530 to 2920/1000 m³ of wastewater treated.

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APPENDIX A

PROTOCOL FOR SAMPLE COLLECTION, STORAGE
AND IDENTIFICATION OF PRIORITY POLLUTANTS

U.S. EPA Grant #R807145010

Technology Evaluation for Priority Pollutant Removal
from Dyestuff Manufacture Wastewater

The objective of work element B of the grant is to establish performance characteristics of existing wastewater treatment plants (WTPs) at participating dyestuff manufacturers (PDMs) with respect to the removal, conversion, and/or production of priority pollutants. Initial qualitative and semi-quantitative screening will be accomplished using the following procedures:

- A. Sample collection and preservation: Sample collection procedures are detailed in the attached protocol written for transmittal to D.E.T.O. and PDMs for review and implementation. Samples will be collected at the inlet and outlet of WTPs. Preservatives will be used in the presence of residual chlorine for analysis of purgeables and as prescribed in EPA methods manual EPA-600/4-79-020 for inorganics and traditional parameters. All samples will be iced during transport and stored at 4°C until analysis. Compositing of grab samples will be performed after return to ESE using flow proportional mixing where possible or simple compositing when flow information is not available.
- B. Sample analysis
 1. Purgeables, base-neutral and acid extractables, direct injectables, and pesticides: Analysis will be performed using EPA method 624 or 625 with the following exceptions and method choices:
 - a. Samples will be analyzed within 30 days of collection and stored at 4°C in the interim. Analysis of purgeables will be performed first.
 - b. Internal standardization technique will be used for quantification and recovery analysis. Specific compound recovery efficiencies will be evaluated only for those priority pollutants identified in the initial screening.
 - c. Quality assurance and quality control procedures for screening analyses will be followed as per EPA-EMSL publication of June 1979, with quarterly analyses of EMSL performance evaluation samples.

Any further modifications of the sampling or analytical plan will be submitted for EPA approval. Upon receiving favorable approval of the above plan, the sampling protocol will be submitted to DETO for implementation.

SAMPLING PROCEDURES FOR SCREENING PHASE

I. Introduction

The initial characterization (screening) of the varied industrial discharges covered by this program will be made on an analysis of a composite effluent sample. Any scheme for collecting a composite sample is, in effect, a method for mechanically integrating to obtain average characteristics of a discharge. During the screening phase, the sample composite can be used to determine the average characteristics that are representative of that discharge. Simple composite samples are those that are made up of a series of aliquots of constant volume collected at regular time intervals in a single container. Some situations may require flow or time proportional sampling. The determination of simple or proportional compositing for periods of 24, 48, or 72 hours will be made on a case-by-case basis, preferably with consultation with Environmental Systems Engineering, Clemson University (ESE). The duration of compositing will depend on the type of sample being collected, the type of facility being sampled, and the time varying characteristics of the discharge. Longer compositing periods are warranted when less stable unit process operations are being sampled. All samples and blanks must be carefully identified as outlined in section II and III of this protocol using water-proof labels and water-proof ink.

II. Sample Collection, Preservation and Handling for the Extractable Organics

II.1: Collection of Grab Samples for Compositing

Representative samples for compositing are to be collected from the manufacturing plant discharge and the final waste treatment plant discharge (effluent of secondary or tertiary treatment, whichever is applicable) for the specified sampling period. The determination of

compositing period -- 24, 48, or 72 hours -- and sampling interval will be made on a case-by-case basis. Prewashed (as per section II.4.3) glass sampling bottles (minimum volume 100 ml) will be provided by ESE. Sample bottles must be filled and sealed according to section III.4. Compositing will be performed by ESE. All samples must be carefully identified using labels supplied by ESE. The following information must be clearly printed using water-proof ink:

- a. Date and time sample collected
- b. Sample number
- c. Sampling location (clearly identifiable on WTP flow sheet to be supplied to ESE)
- d. Name of person collecting sample
- e. Comments (important circumstances, variances, etc.).

Each sample must be refrigerated at 4°C or iced until pick-up by an ESE representative. If at all possible, a flow chart recording or hourly totalizer reading for the sampling period shall be recorded and given to the ESE representative at the scheduled sample pick-up time.

II.2. Field Blank Procedure for the Manual Composite Sample

Blank water, i.e., ESE supplied laboratory cleaned organic free water will be added to prelabeled sample bottles, shipped to the sampling sites, and returned for analysis exactly as the samples.

II.3. Automated Sampling for Extractable Organics

II.3.1: Automated sampling may be substituted if desired by manufacturing plant personnel provided sampling equipment required by this section is provided by the manufacturing plant and procedures used meet the following criteria and is approved by ESE.

- II.3.2: Each PDM will collect a representative composite sample from the manufacturing plant discharge and the final waste treatment plant discharge (effluent of secondary or tertiary treatment, whichever applicable). The maximum time interval between aliquot samples shall be no longer than 30 minutes. The minimum aliquot size shall be 100 ml. Minimum composite volume shall be 2-1/2 gallons.
- II.3.3: Automatic Sampler - A peristaltic pump automatic sampler with timer and a single glass compositing jug is required. The 2-1/2 - 3 gallon compositing bottle must be glass and cleaned as outlined below. New unused tubing must be used for the sampling line and for the pump for each individual outfall or sampling location. Vacuum type automatic samplers may be used provided that the sample chambers are glass and that they are cleaned after every use as outlined for glass composite containers. The sampler or composite container must be kept in an insulated chest with ice to maintain the sample at 4°C during the compositing procedure. At the completion of the compositing period, the container must be sealed with a Teflon lined cap and stored at 4°C until pick-up by an ESE representative.
- II.3.4: If raw untreated industrial discharges which are high in suspended solids are to be sampled, then it is imperative that adequate sample flow rate be maintained throughout the sample train in order to effectively transport the solids. In horizontal runs, the velocity must exceed the scour velocity, while in vertical runs the settling or the fall velocity

must be exceeded several times to assure adequate transport of solids in the flow. The equipment used in sampling raw discharges then must have a minimum intake velocity of 60 cm per second (2 fps). In the sampling of treated effluents, just about any commercially available automatic liquid sampler could be used.

II.4. Field Blank Procedure for Automatic Samplers

II.4.1: Blank water, i.e., ESE supplied laboratory cleaned organic free water can be supplied upon request in bulk glass containers (approximately ten liters) for field use with automatic samplers. ESE will analyze the blank water to determine the organic background that may be present.

II.4.2: Procedure - All parts of the sampling system must be scrubbed with hot detergent water and thoroughly rinsed with tap water and blank water prior to use. Further rinsing with methylene chloride is required when parts permit, i.e., are not susceptible to dissolution by the solvent. (Note: Tygon plastic tubing is a source of phthalate ester contamination. Where its use is required, i.e., in the peristaltic pump, the length must be kept as short as possible). Teflon is acceptable and may be used in other parts of the sampling system as in intake lines. In the field, two liters of blank water must be pumped through the sampling line and pump tubing and discarded. Then three liters of blank water should be pumped through the system and collected as a blank in a 1-gallon sample bottle that has been prepared as described below, sealed with Teflon lined cap, and immediately

iced or stored at 4°C until pick-up by an ESE representative.

II.4.3: Preparation of Glass Sample Bottles - Glass sample bottles must be prepared for use by washing with hot detergent water and thoroughly rinsing with tap water and blank water. The bottles must be heated at 400°C in a muffle-furnace or dry heat sterilizer for 30 minutes or, alternatively rinsed with methylene chloride and air dried at room temperature protected from atmospheric or other sources of contamination. Caps for the bottles must be lined with Teflon which has been solvent rinsed as above.

III: Volatile Organics (Purgeables)

III.1: Containers - 40 ml screw cap glass vials with Teflon faced silicone septa will be supplied by ESE.

III.2: Sample bottles shall have been prepared by ESE per the following:
Bottles, septa, and caps will be washed with hot water and thoroughly rinsed with tap water and blank water, heated at 105°C for one hour (except caps), and cooled to room temperature in an enclosed contaminant-free area. When cool, bottles will be sealed with septa (Teflon side down) and screw cap. Each PDM must maintain the bottles in this condition until just prior to filling.

III.3: Collect duplicate samples each time purgeable samples are collected. If preservation for residual chlorine is to be used, (as determined by consultation with ESE) collect four samples during each sampling period. Two should be preserved and two not preserved. Two preserved and two nonpreserved blanks are also to be provided by ESE and handled as a sample by the PDM.

III.4: Filling and Sealing Bottles - Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum (Teflon side down) on the convex sample meniscus. Seal the sample with the screw cap. To ensure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The absence of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal. The sample must remain hermetically sealed until it is analyzed.

III.5: Field Blank Procedure for Volatile Organics (Purgeables) - Blank water, i.e., ESE supplied laboratory cleaned organic free water will be added to pre-labeled vials, shipped to the sampling sites, and returned for analysis exactly as the samples.

III.6: Preservation of Volatile Organics - Preservative (sodium thiosulfate or sodium bisulfite) is used to stabilize samples containing residual chlorine. The production of chloroform and other haloforms continues in such samples if they are not stabilized. Waste streams that have been treated with chlorine should be tested on-site to determine whether or not residual chlorine is present, indicating preservative is needed. If preservation is required, collect both preserved and non-preserved samples as per section III.3. Store samples at 4°C or in ice until pick-up by an ESE representative.

IV. Sample Collection for Traditional Parameters Analyses

Traditional parameters (TOC, pH, etc.) will be measured in an aliquot of the samples collected for extractables analyses after compositing by ESE.

V. Sample Collection for Inorganics Analyses

V.1: Containers for Inorganics Samples

Samples for inorganics analyses (trace metals) shall be collected in polyethylene bottles provided and prepared by ESE by leaching for two days in 10% HNO_3 followed by exhaustive rinsing with deionized water.

V.2: Sample Collection

Samples shall be collected at the same times as samples for extractables analyses. An approximate 10 ml headspace should be left in each bottle to allow for acid addition.

V.3: Sample Preservation

ESE personnel will acidify each sample to $\text{pH} < 2$ with redistilled HNO_3 before transport to ESE.

V.4: Compositing

Each PDM will composite samples for inorganics analyses as described below:

A one-gallon and an eight-ounce nalgene container will be supplied to each PDM for each outfall to be sampled. An eight-ounce sample must be collected at specified intervals during the sampling period. Each sample is to be transferred to the refrigerated one-gallon compositing container immediately after sample collection. The composite sample must be stored at 4°C or on ice until pick-up by an ESE representative.

PROCEDURE FOR COLLECTION, HANDLING, AND STORAGE
OF SAMPLES FROM DYESTUFF MANUFACTURE WASTEWATER

U.S. EPA Grant #R807145010

Technology Evaluation for Priority Pollutant
Removal from Dyestuff Manufacture Wastewater

I. INTRODUCTION

Sampling will be performed by participating dye manufacturers's (PDMs) plant personnel using containers supplied by Environmental Systems Engineering (ESE). The general plan is to collect wastewater samples for extractables, purgeables and metals analysis in three different containers at each specified sampling location at each PDM's waste treatment plant. Sampling containers will be dropped off and picked up by an ESE representative and returned to Clemson for analysis. A summary of sampling details is listed in Table 1.

II. SAMPLING DETAILS

II.1. Scheduled sampling dates are: _____

II.2. Specified sampling locations are as follow:

II.2.1. Influent _____

II.2.2. Effluent _____

II.2.3. Additional location (if applicable) _____

II.3. Sample for Extractables

II.3.1. _____ and _____ wastewater samples must be collected every _____ hours for a sampling period of _____ hours.

II.3.2. ESE will provide enough sample bottles plus a few extras to collect required samples. Sample bottles are 1-quart amber glass bottles. Sample bottles have been pre-cleaned and sealed and must remain sealed until sample is collected.

II.3.3. Each bottle will be pre-labeled by ESE with spaces for the following:

- sample for extractables
- date
- location
- number
- name of person sampling

(specifics must be filled in by plant personnel responsible for sample collection.)

II.3.4. At the beginning of the specified sampling period and every _____ hours thereafter until the end of the sampling period, a 1-quart sample of wastewater must be collected at each of the above specified locations.

II.3.5. Fill sample bottle to overflowing and seal with the teflon-lined cap provided.

II.3.6. Do not add any preservative to the sample; just seal and fill in blanks on label.

II.3.7. Immediately refrigerate the sample at 4°C, or maintain in ice, until pick-up by an ESE representative.

II.4. Sample for Purgeables

II.4.1. _____ and _____ waste-water samples must be collected every 12 hours for a sampling period of _____ hours.

II.4.2. ESE will provide enough sample containers plus a few extras to collect the required number of samples. Sample containers are 40 ml screw cap vials fitted with teflon lined septa. Sample vials have been precleaned and sealed and must remain sealed until sample pick-up by an ESE representative.

II.4.3. Each vial will be pre-labeled by ESE with spaces for:

- sample for purgeables
- date
- location
- number
- name of person sampling

(specifics must be filled in by plant personnel responsible for sample collection.)

II.4.4. At the beginning of the specified sampling period and every 12 hours thereafter until the end of the sampling period, duplicate samples must be collected at each of the above specified locations.

II.4.5. If the waste treatment plant effluent has residual chlorine, four samples must be collected every 12 hours at that location. Two of the four samples must be preserved and two not preserved.

II.4.6. Samples to be preserved must be preserved by adding 10 mg of sodium chrosulfate per 40 ml of wastewater sample. This should be done immediately after collecting the grab sample prior to sealing the vial.

II.4.7. Filling the sample vial - Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum (Teflon side down) on the convex sample meniscus. Seal the sample with the screw cap. To ensure that the sample has been properly sealed, invert the vial containing the sample and lightly tap the lid on a solid surface. The absence of trapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal. The sample must remain sealed until it is analyzed.

II.4.8. Immediately refrigerate the sample at 4°C or maintain in ice until pick-up by an ESE representative.

II.5. Sample for Metals Analysis

II.5.1. _____ and _____ wastewater samples must be collected every _____ hours for a sampling period of _____ hours.

II.5.2. ESE will provide the required number of composite containers and grab sample bottles. Each PDM will receive 1 compositing bottle and 1 grab sample bottle for each

sampling location specified above. The compositing bottle will be a 1-gallon nalgene bottle. The grab sampling bottle will be an 8-ounce nalgene bottle. These containers have been pre-cleaned and must not be rewashed by plant personnel.

II.5.3. Each set of sampling bottles will be pre-labeled by ESE with spaces for:

- sample for metals analysis
- date
- location
- name of person sampling

(Specifics must be filled in at the time of sampling by plant personnel responsible for sample collection.)

II.5.4. At the beginning of the specified sampling period and every _____ hours thereafter until the end of the sampling period, one 8-ounce bottle must be collected and immediately transferred to the 1-gallon compositing bottle. These samples are to be collected at each of the above specified locations. Remember composite and grab sample bottles have identical labels and must be used in pairs.

II.5.5. After collecting the grab sample in the 8-ounce nalgene bottle it will be necessary to thoroughly rinse the 8-ounce bottle with distilled-deionized water and reseal until the next scheduled sample is to be taken.

II.5.6. Do not add any preservative to the sample.

II.5.7. Cap the 1-gallon bottle with the nalgene cap provided.

II.5.8. Immediately refrigerate the sample at 4°C or maintain in ice until pick-up by an ESE representative.

II.6. Field Blanks

II.6.1. Field blanks for extractables - Two pre-filled, pre-labeled field blanks will be delivered to the sampling site (each PDM) in 1-quart amber glass bottles along with sampling bottles. Field blanks must not be opened and must be handled the same as wastewater samples, i.e., kept refrigerated and returned to Clemson for analysis.

II.6.2. Field blank for purgeables

II.6.2.1. Influent - Two pre-filled, pre-labeled field blanks will be delivered to the sampling site in 40 ml vials along with sampling vials. Field blanks must not be opened and must be handled the same as samples.

II.6.2.2. Effluent - Four pre-filled, pre-labeled field blanks will be delivered to the sampling site in 40 ml vials along with sampling vials and must be handled as outlined in section II.6.2.1.

II.6.3. Field blank for metals - None required.

II.7. Grab Samples

II.7.1. All samples collected for extractable, purgeable and metals analysis discussed in the preceding sections are to be grab samples. Collect grab samples from mid-channel at mid-depth. Samples should be collected at a turbulent, well-mixed section of the channel.

II.8. Automatic Sample Collection

II.8.1. Should any PDM choose to use an automated sampler, it will be necessary to contact John Coates, Environmental Systems Engineering Department, Clemson University, (803)656-3276 to obtain a copy of the approved procedure.

III. ADDITIONAL INFORMATION AND DATA

III.1. Flow Data - Each PDM is requested to forward to ESE influent and effluent flow charts coincident with the sampling period. Charts should be given to the ESE representative at the time samples are picked up.

III.2. Problems Experienced/Comments

Problems experienced, unusual circumstances regarding sample collection or waste treatment, extreme variances in flow and/or organic loads during the sampling period should be noted, discussed and forwarded to:

John Coates
Environmental Systems Engineering
401 Rhodes Research Center
Clemson University
Clemson, SC 29631

TABLE I. SUMMARY OF SAMPLING DETAILS

Item	Samples		
	Extractables	Purgeables	Metals
Container	1-qt. amber glass bottle	40 ml vial	1 gal. nalgene bottle
Volume	1 qt.	40 ml	8 oz. every 6 hrs.
Fill to Top	yes	yes	no
Preservative	no	yes if Cl present	no
Frequency	4/24 hrs.	2/24 hrs.	4/24 hrs.
Duration	48 hrs.	48 hrs.	48 hrs.
Refrigeration	yes	yes	yes
Field Blank Req'd.	yes	yes	no

APPENDIX B

POWDERED ACTIVATED CARBON CHARACTERIZATION

NUCHAR S-A 15

Product Data
Bulletin P-105

DESCRIPTION AND TYPICAL APPLICATIONS

Nuchar S-A 15 is a high activity powdered activated carbon developed specifically for wastewater treatment. Due to its high surface area and large pore volume, it is highly effective for powdered physical-chemical systems, tertiary treatment or the enhancement of biological treatment processes.

SPECIFICATION^{*}

Iodine Number (mg/g)	800 min
Molasses Decolorizing Index	15 min
Moisture, as packed (%)	10 max
pH	4 - 6
Ash (%)	15 max

TYPICAL PROPERTIES⁺⁺

Apparent Density (lbs/cu ft)	24 - 26
Apparent Density (kg/m ³)	385 - 415
Surface Area (Nitrogen BET Method (m ² /g)	1400 - 1800
Total Pore Volume (cm ³ /g)	2.2 - 2.5
Sieve Analysis:	
Thru 100 mesh (%)	95 - 100
Thru 200 mesh (%)	85 - 95
Thru 325 mesh (%)	65 - 85

PACKAGING

Nuchar S-A 15 is available in bulk truck, bulk rail car or in individually shrink-wrapped 45 pound multiwall paper bags on non-returnable, wood pallets.

* Specifications and typical property data using Westvaco procedures.

+ Typical properties are for general information and are not to be construed as purchase specifications.

APPENDIX C

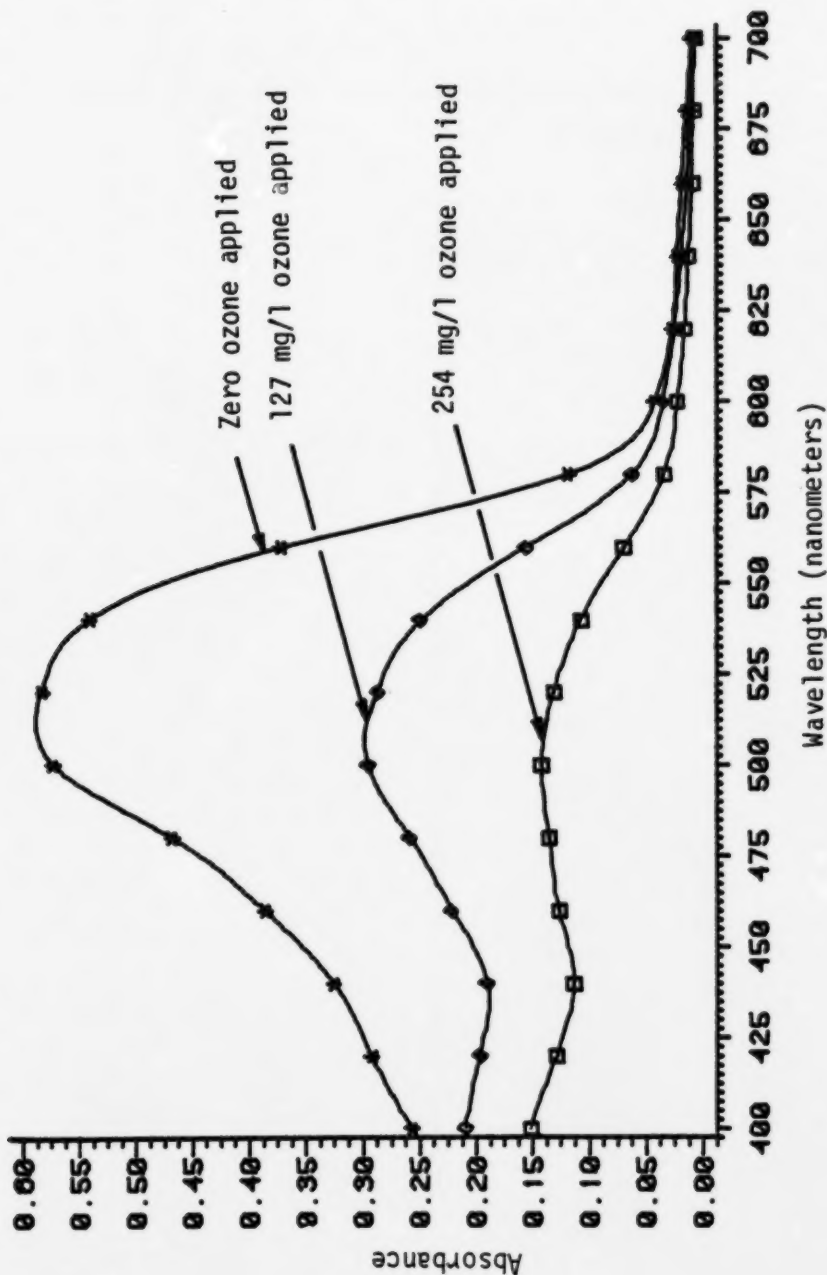


Figure C1. Visible spectral shifts due to ozonation for sample B.

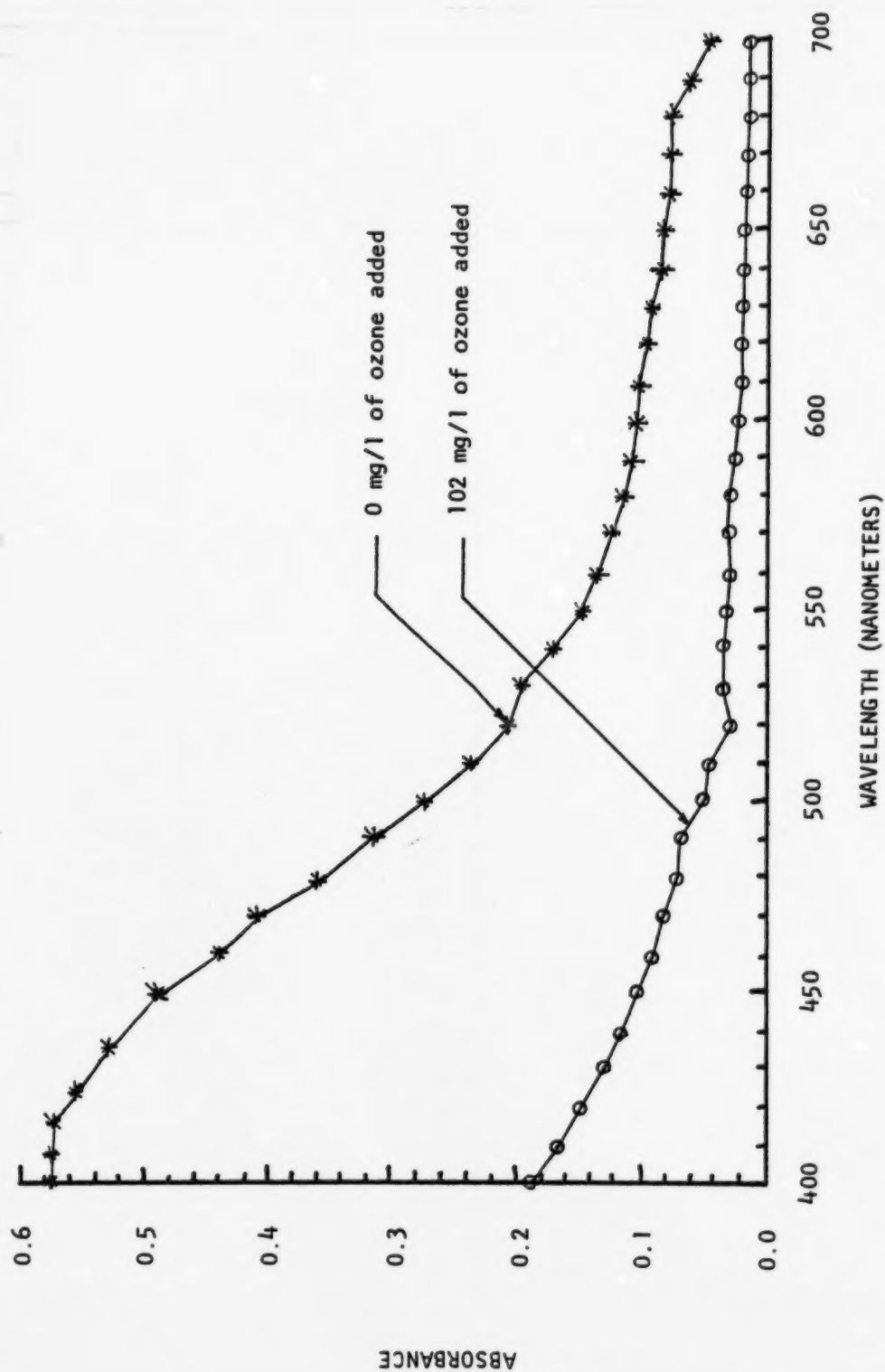


Figure C2. Visible spectral shifts due to ozonation for sample C.

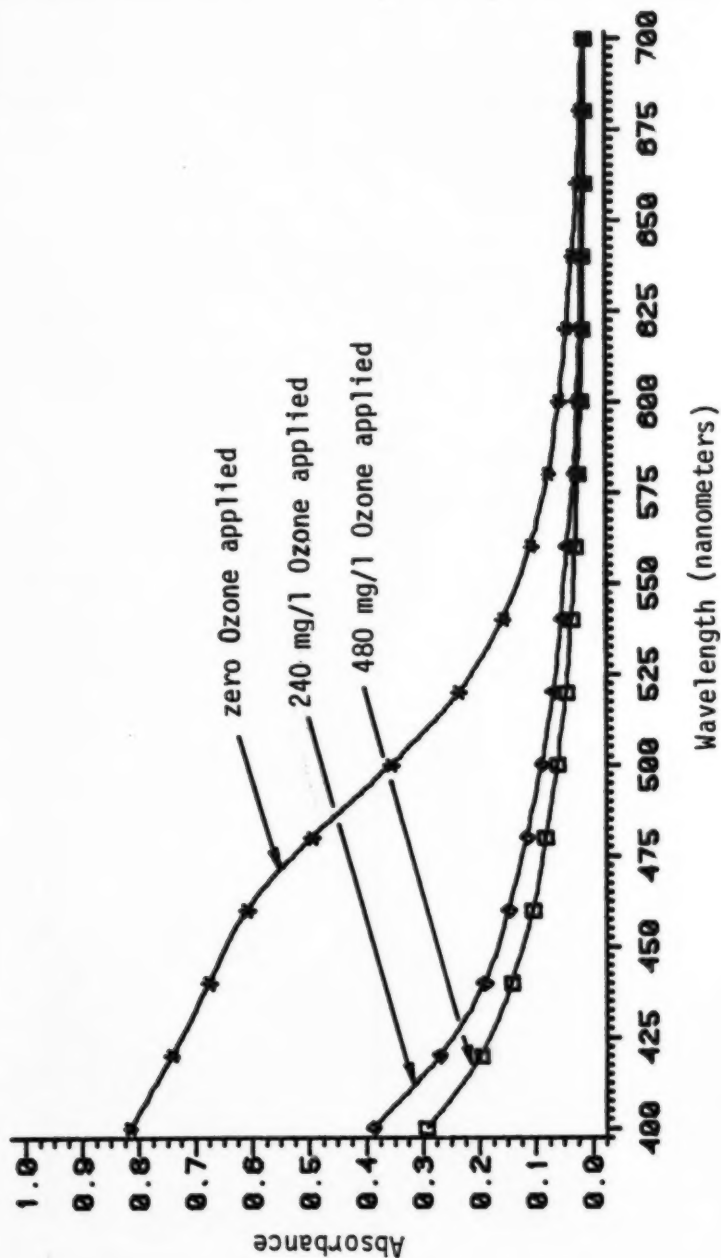


Figure C3. Visible spectral shifts due to ozonation for sample D.

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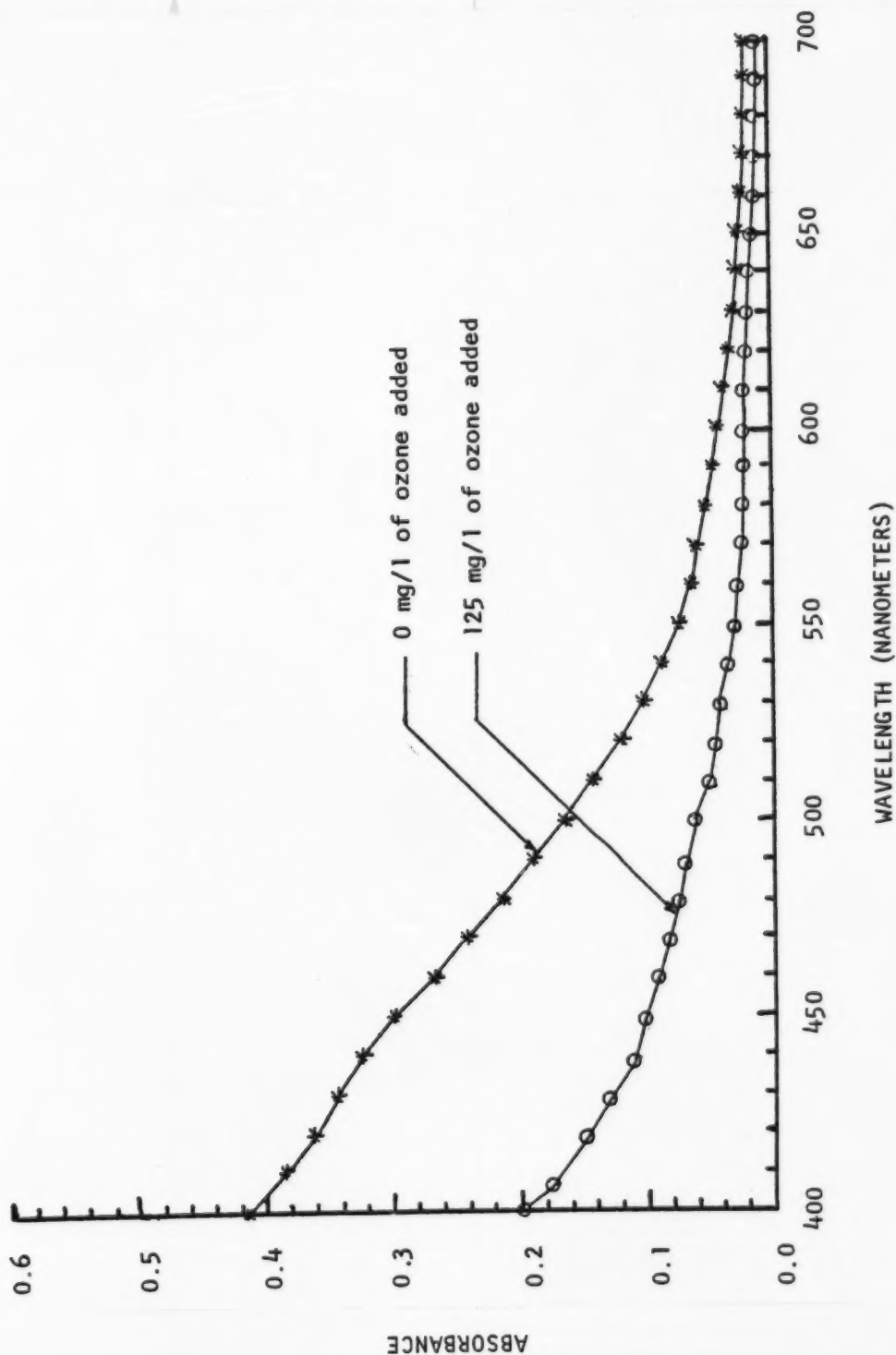


Figure C4. Visible spectral shifts due to ozonation for sample E.

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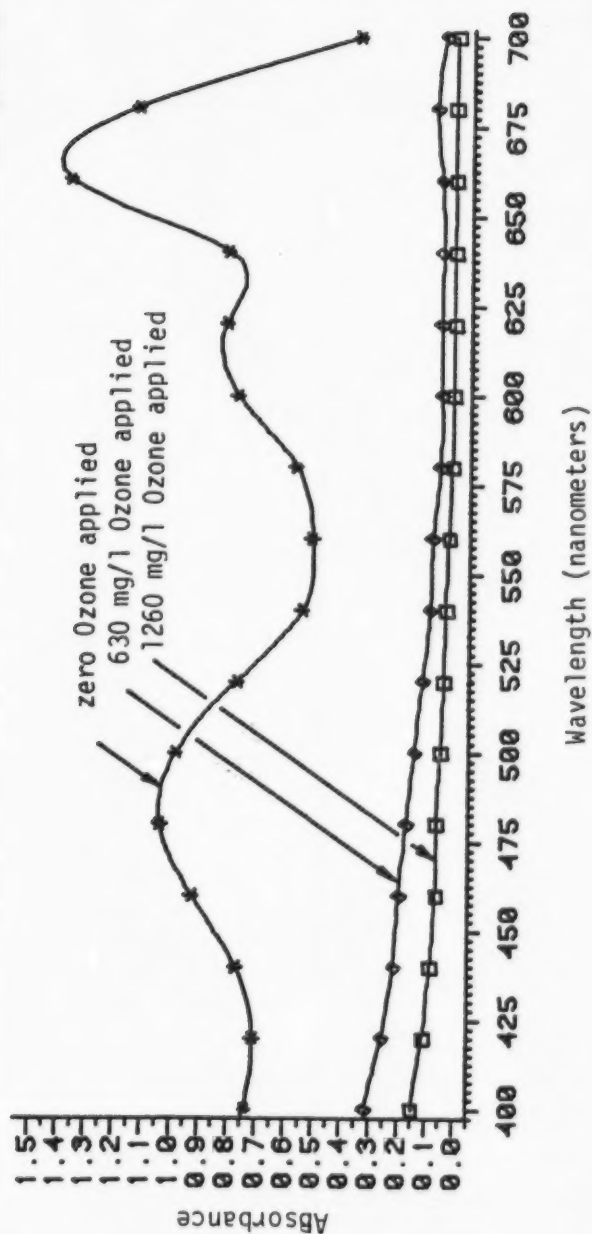


Figure C5. Visible spectral shifts due to ozonation for sample F.

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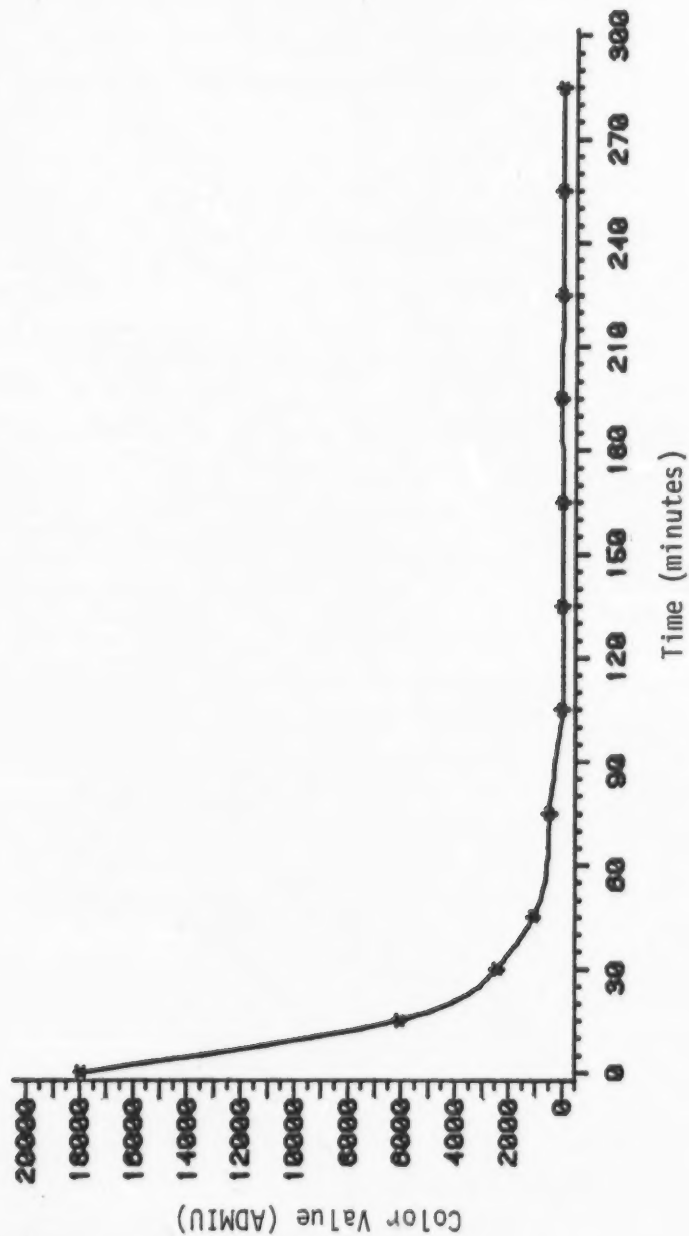


Figure C6. Color value degradation due to ozonolysis for sample B.

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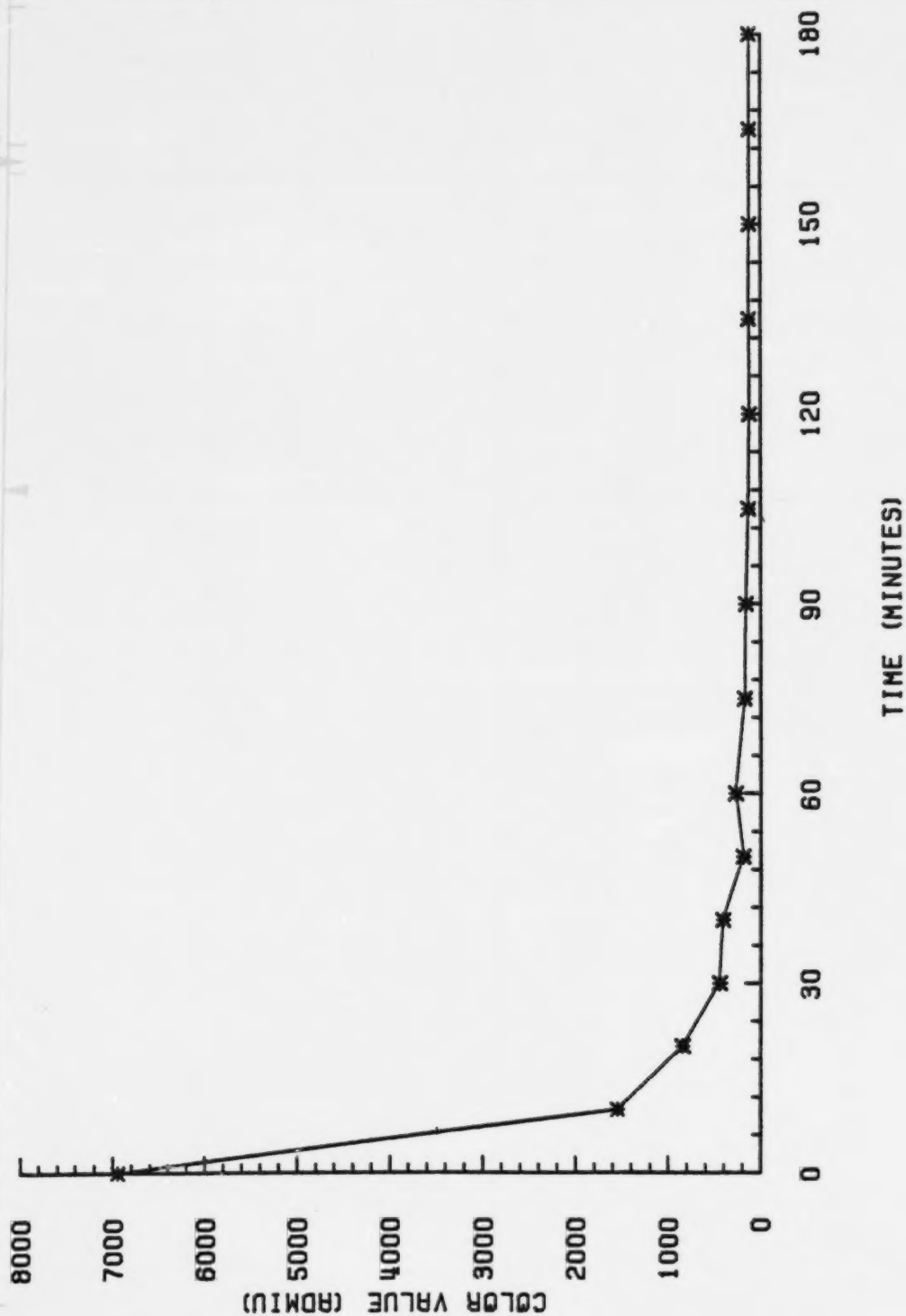


Figure C7. Color value degradation due to ozonolysis for sample C.

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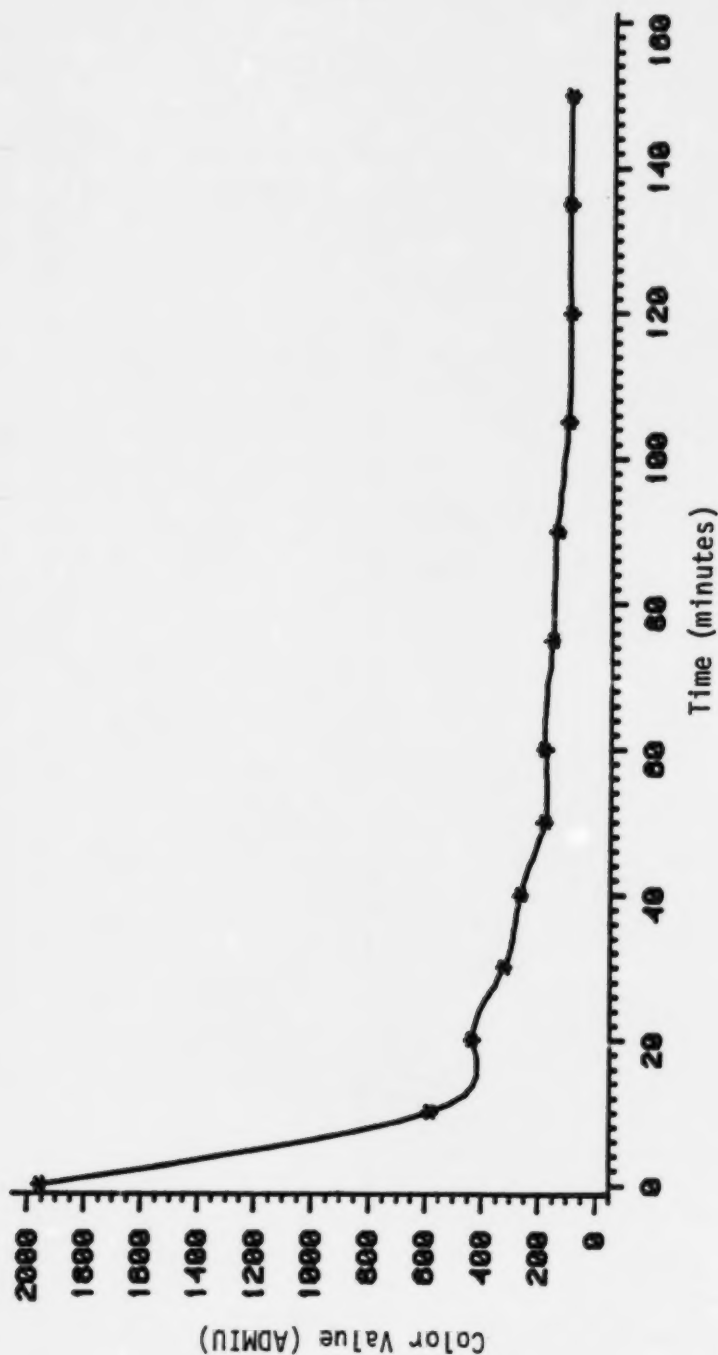


Figure C8. Color value degradation due to ozonolysis for sample D.

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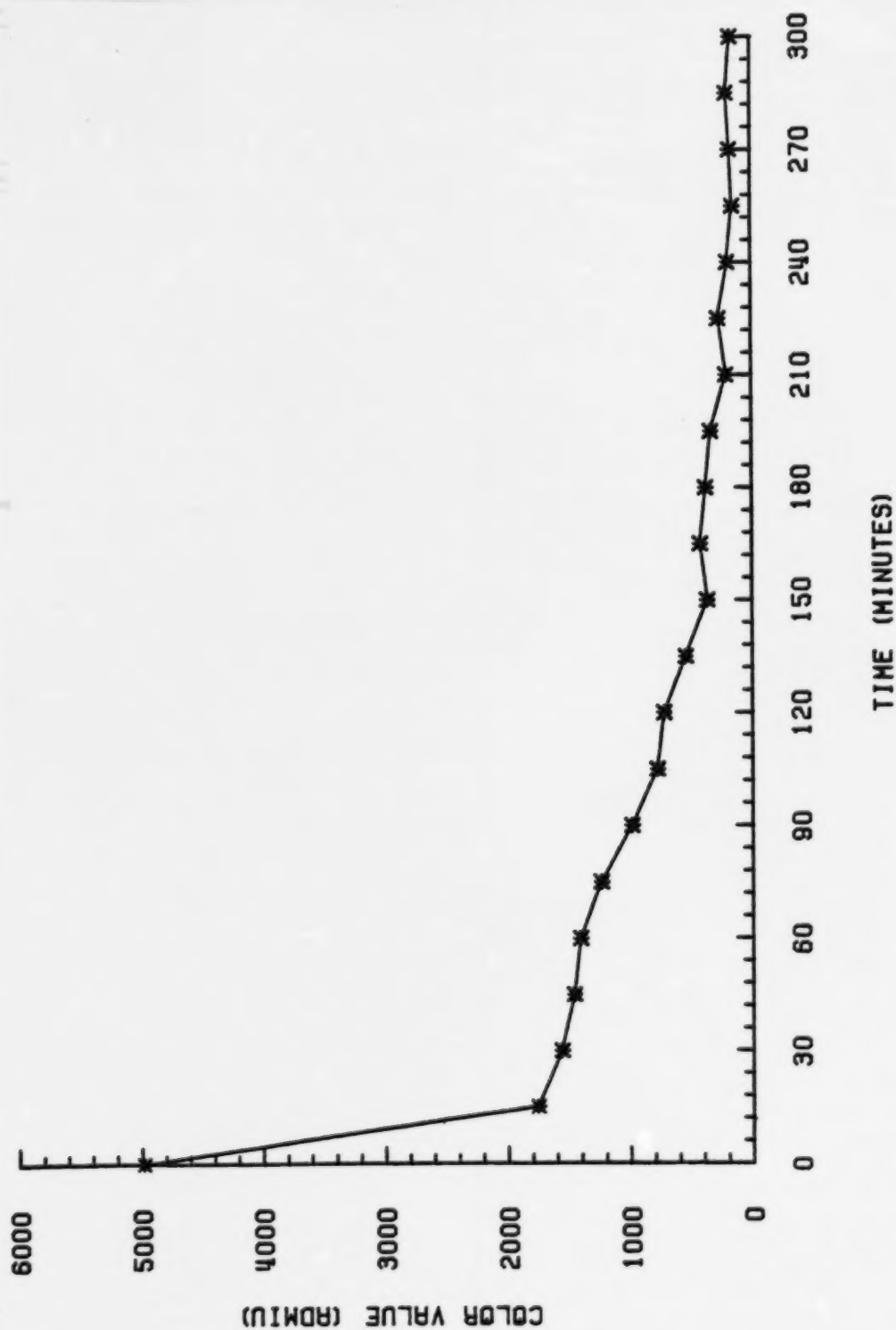
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Figure C9. Color value degradation due to ozonolysis for sample E.

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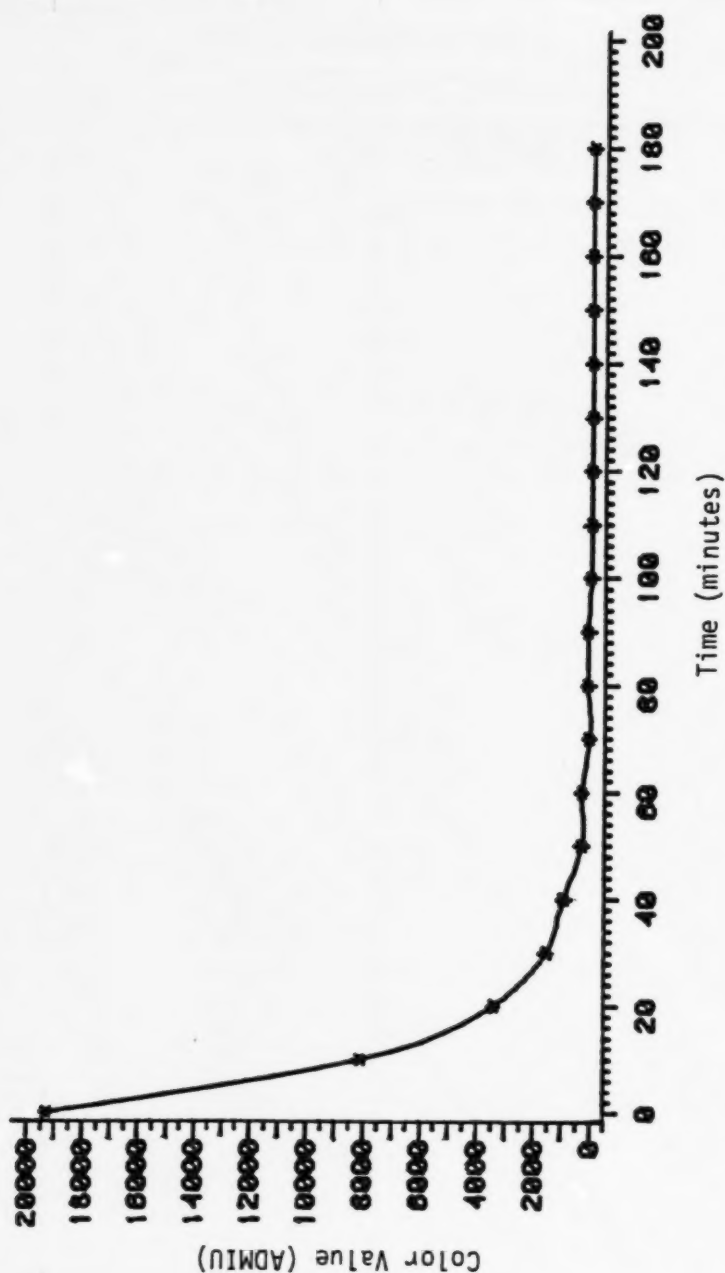


Figure C10. Color value degradation due to ozonolysis for sample F.

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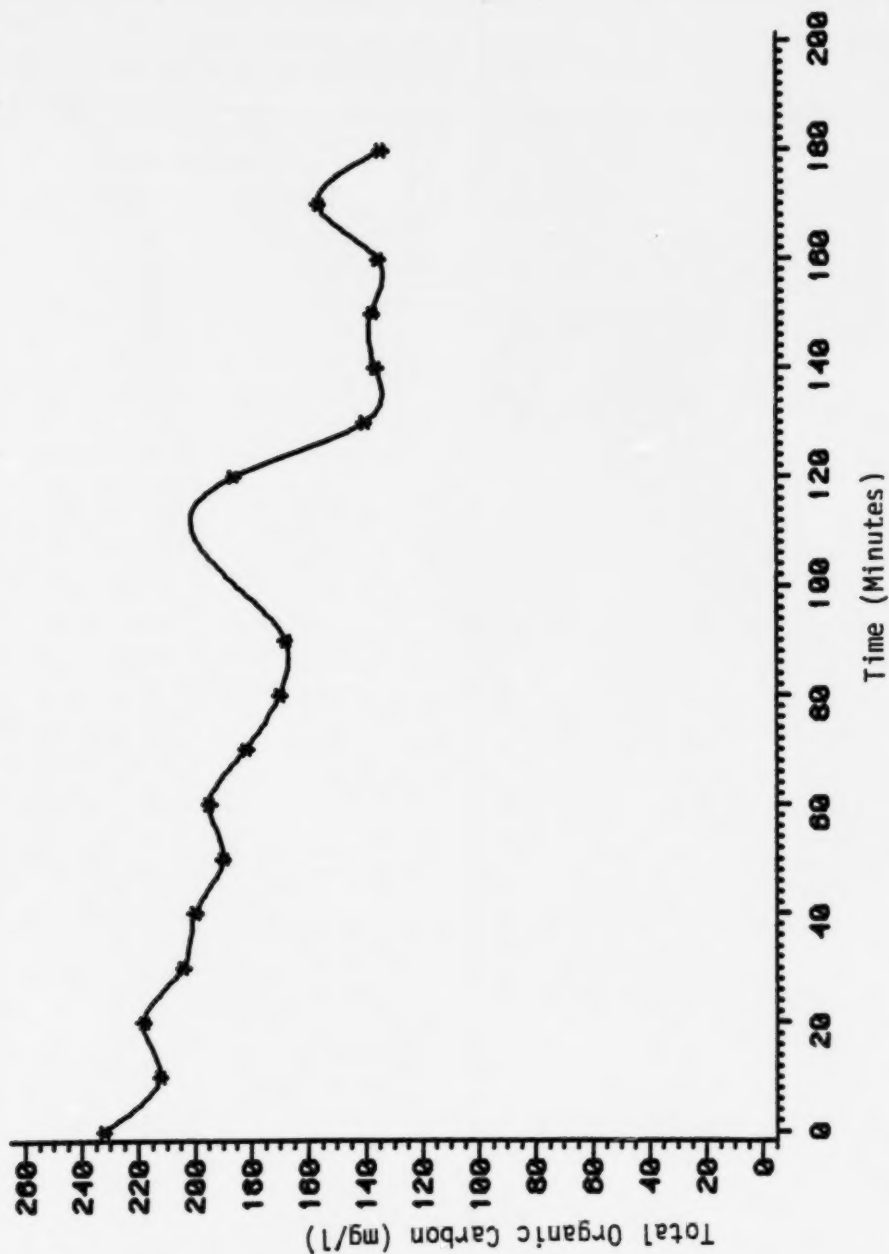


Figure C11. TOC degradation due to ozonolysis for sample B.

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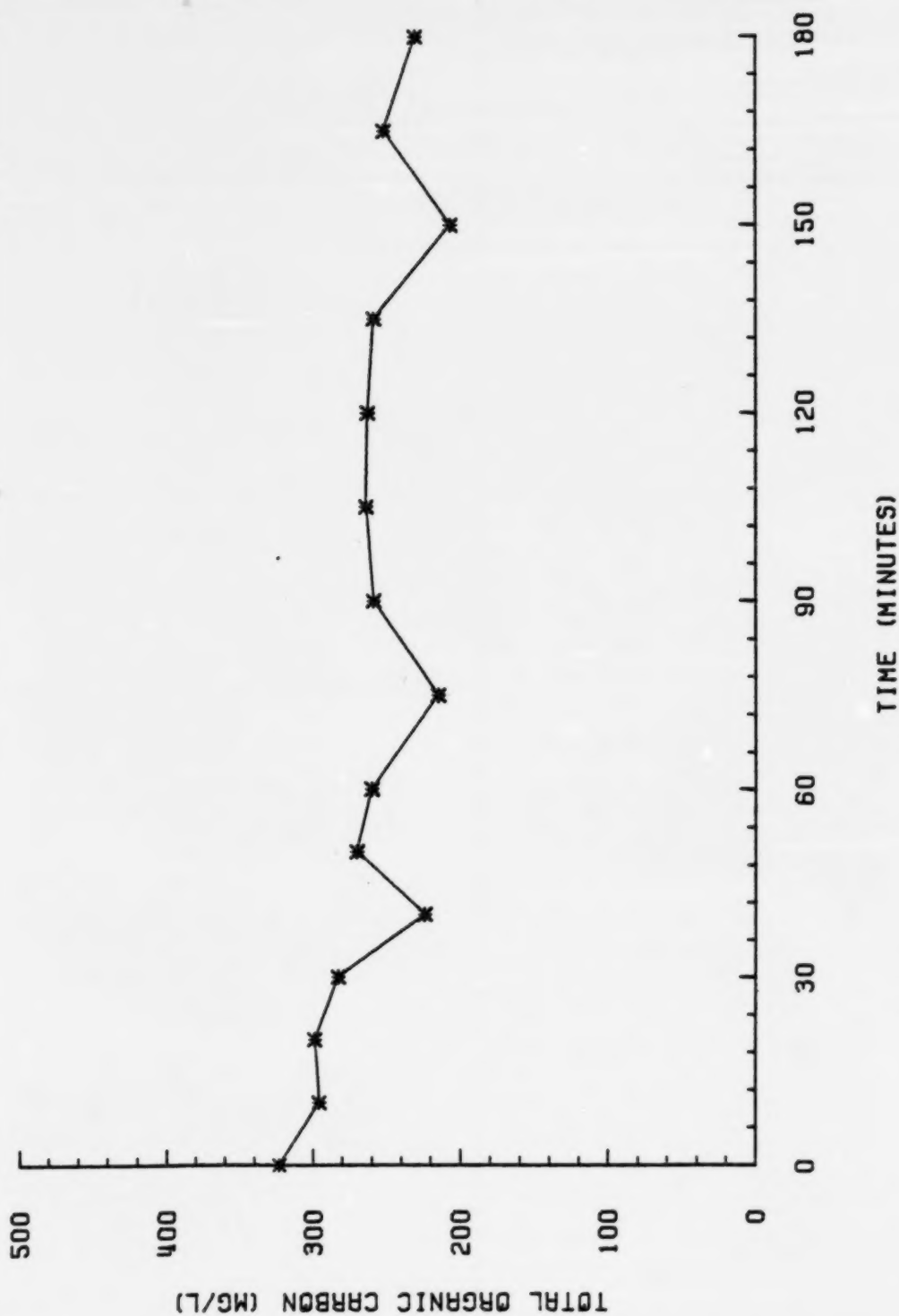


Figure C12. TOC degradation due to ozonolysis for sample C.

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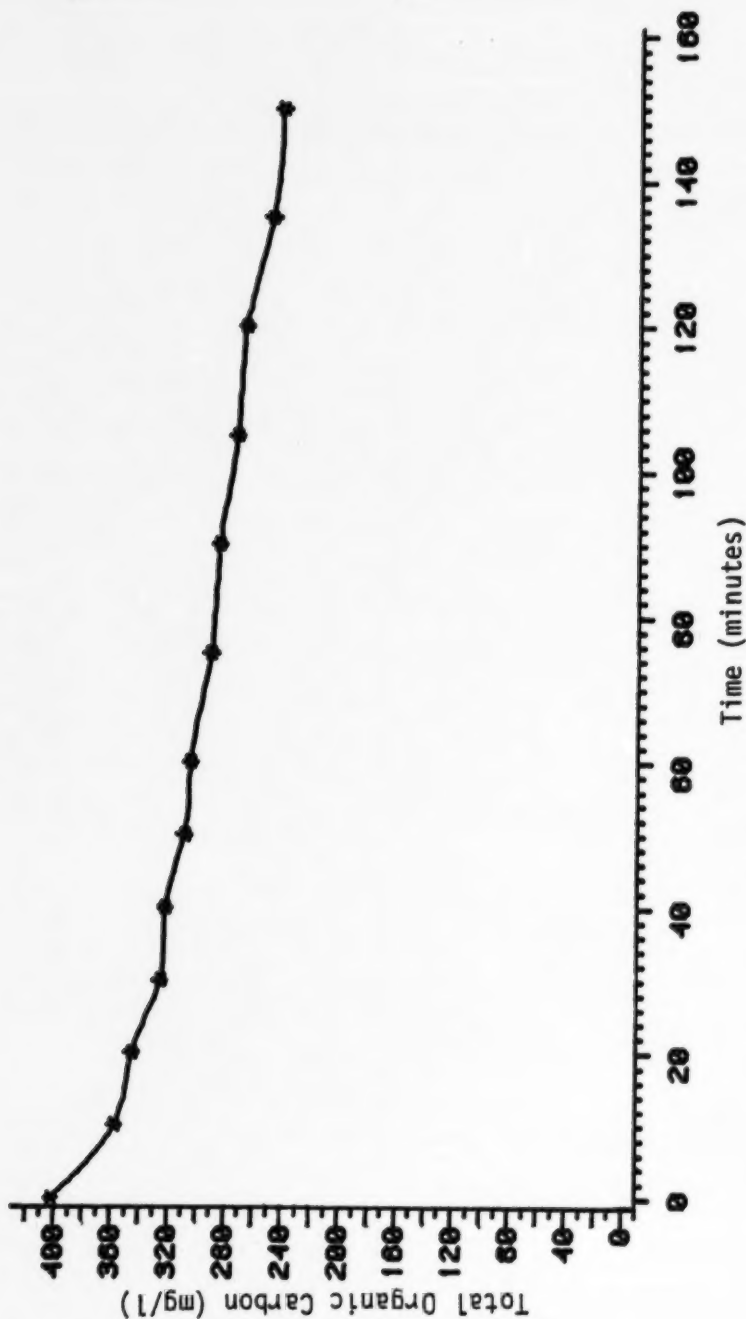


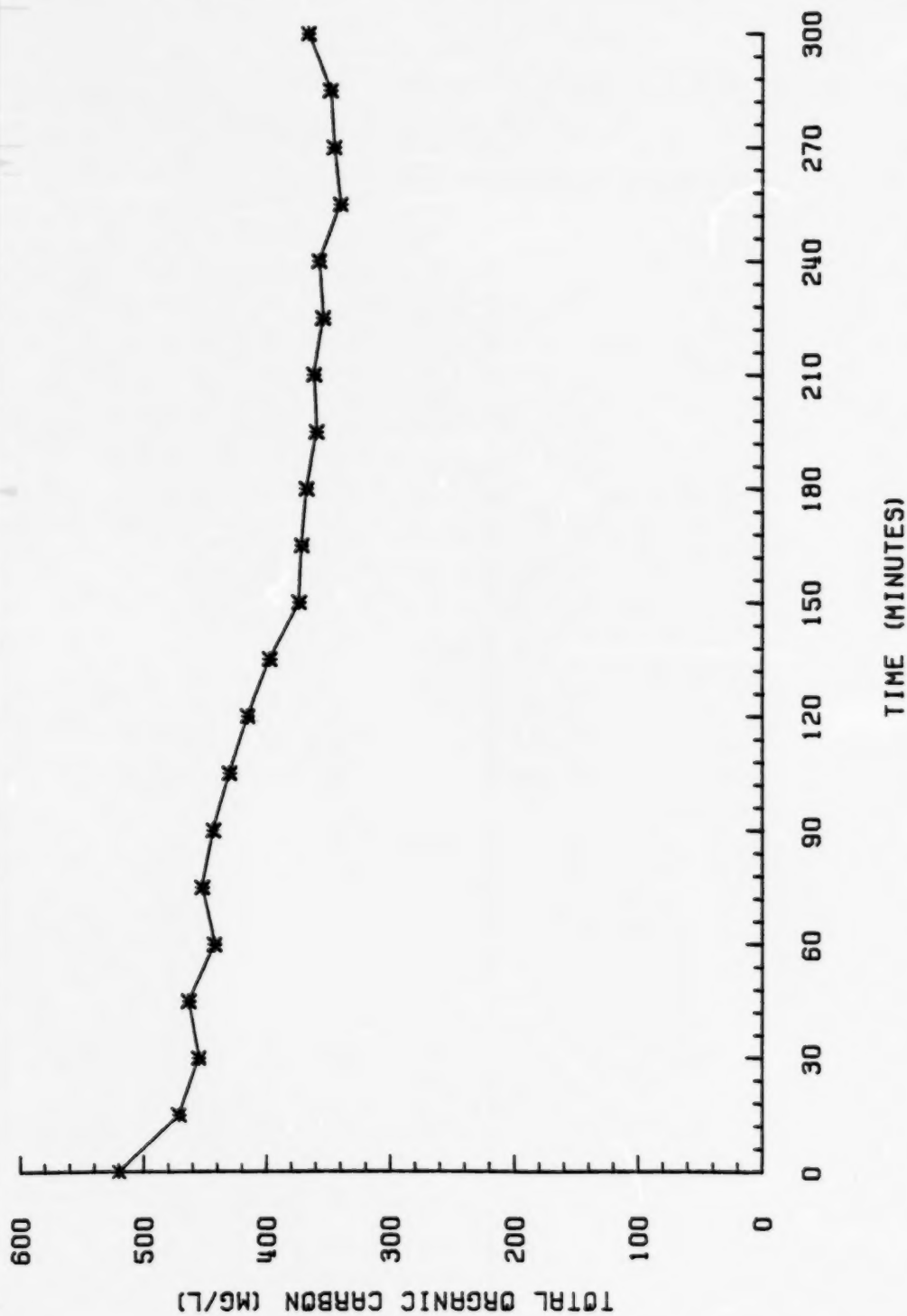
Figure C13. TOC degradation due to ozonolysis for sample D.

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Figure C14. TOC degradation due to ozonolysis for sample E.

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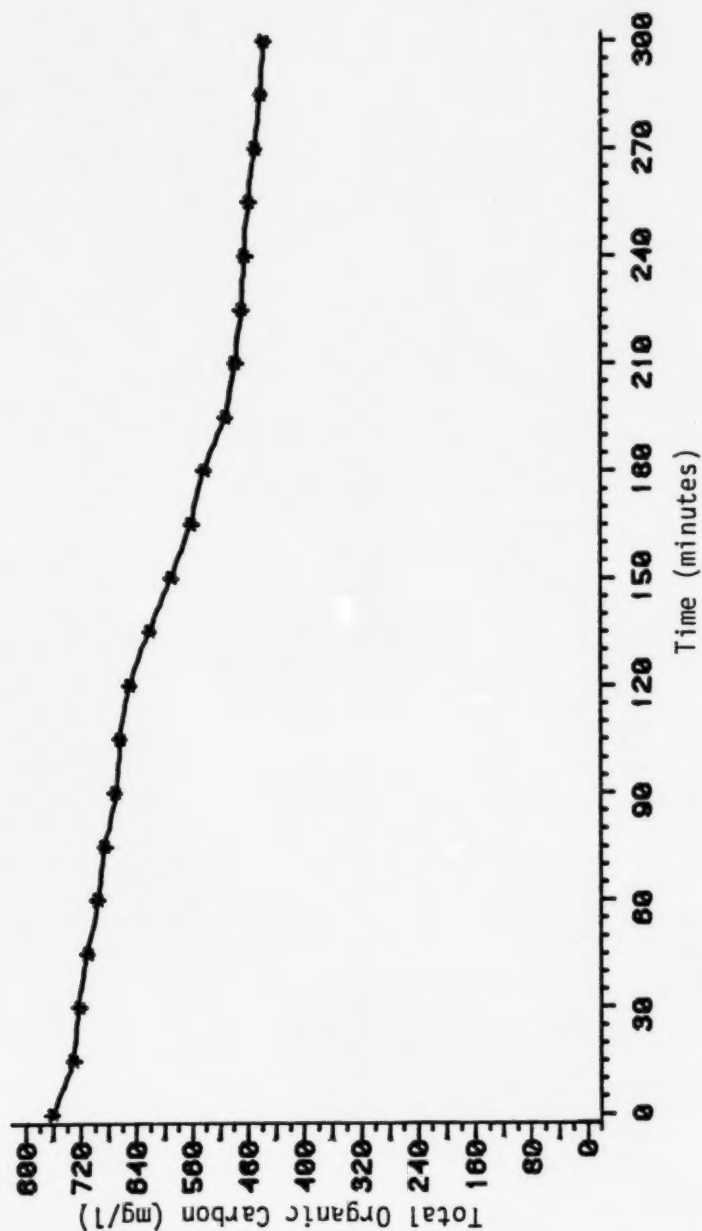


Figure C15. TOC degradation due to ozonolysis for sample F.

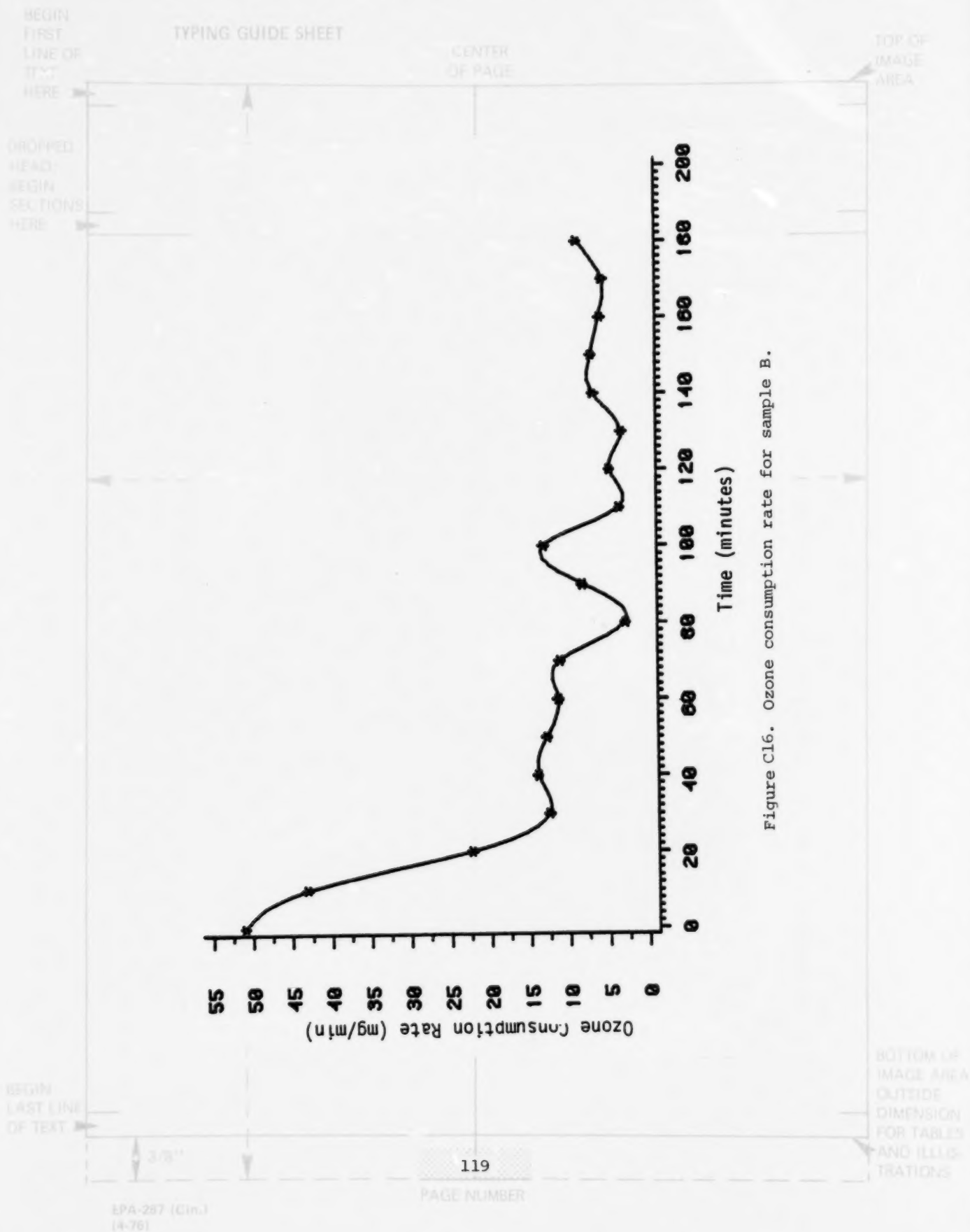


Figure Cl6. Ozone consumption rate for sample B.

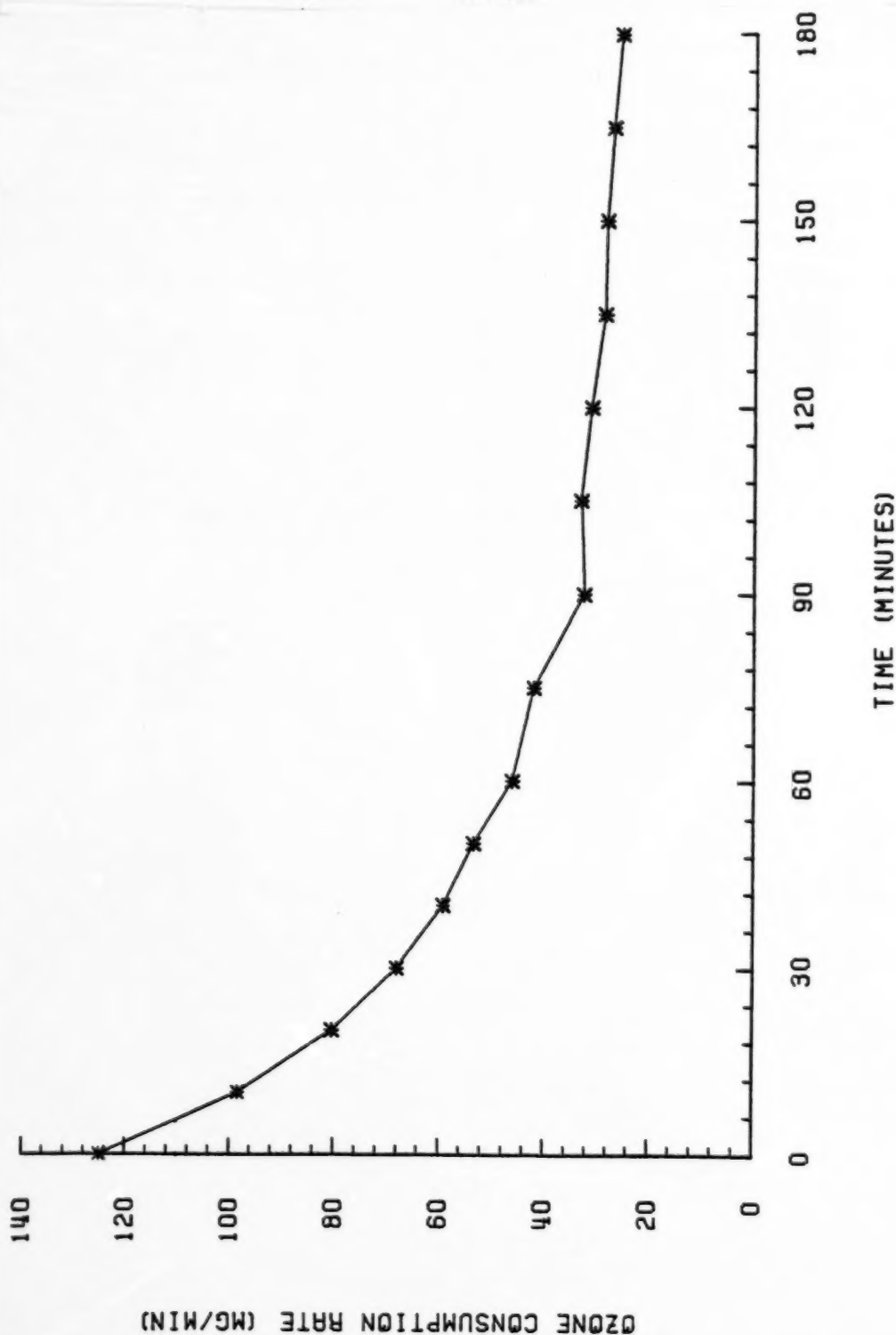
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Figure C17. Ozone consumption rate for sample C.

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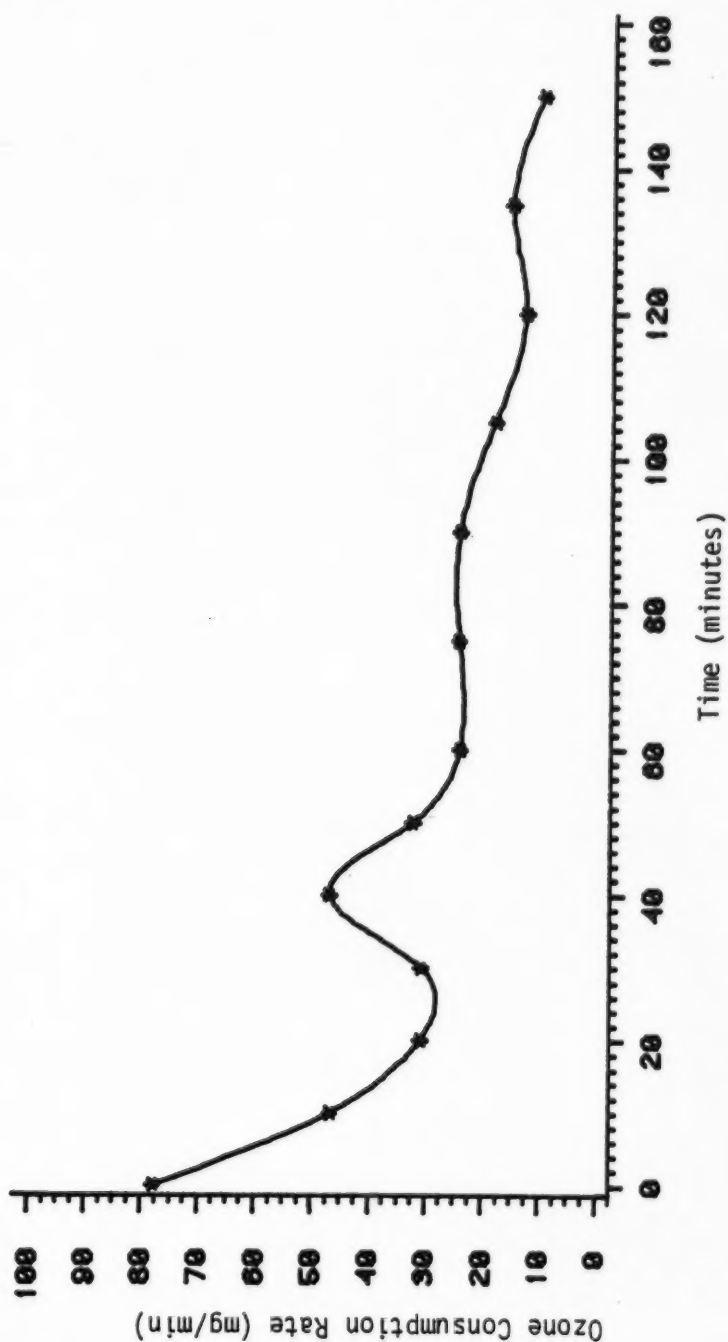


Figure C18. Ozone consumption rate for sample D.

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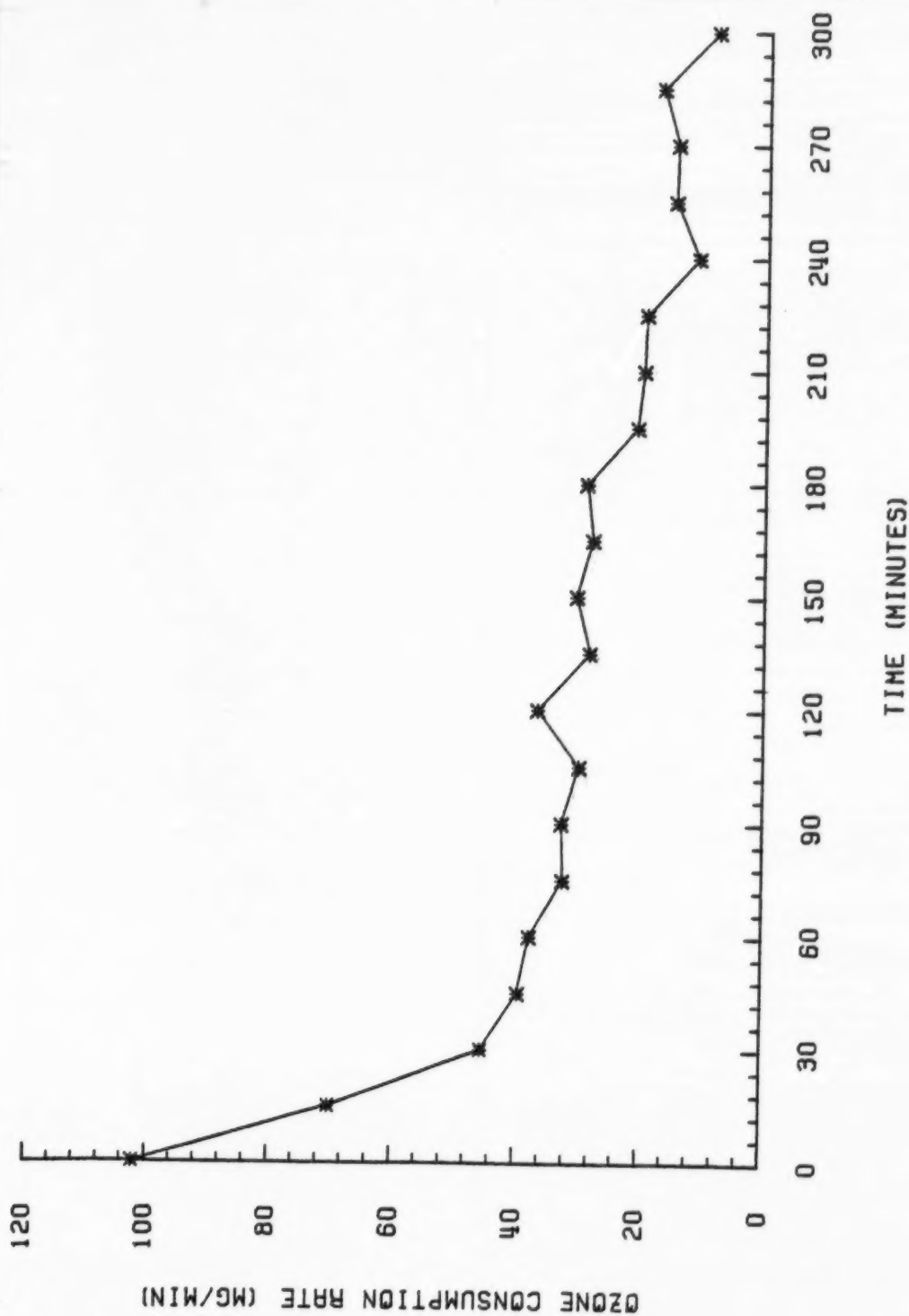


Figure C19. Ozone consumption rate for sample E.

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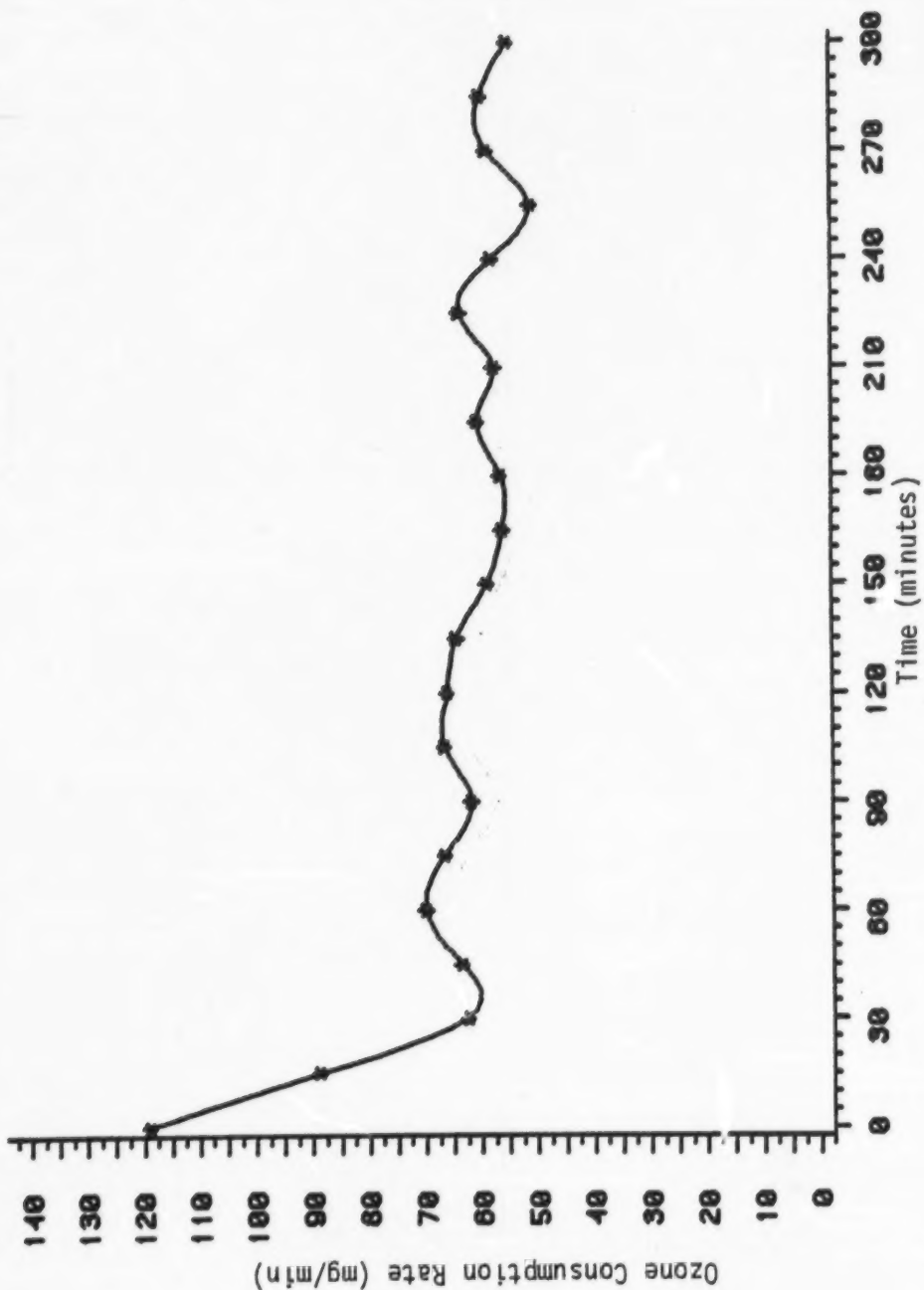


Figure C20. Ozone consumption rate for sample F.

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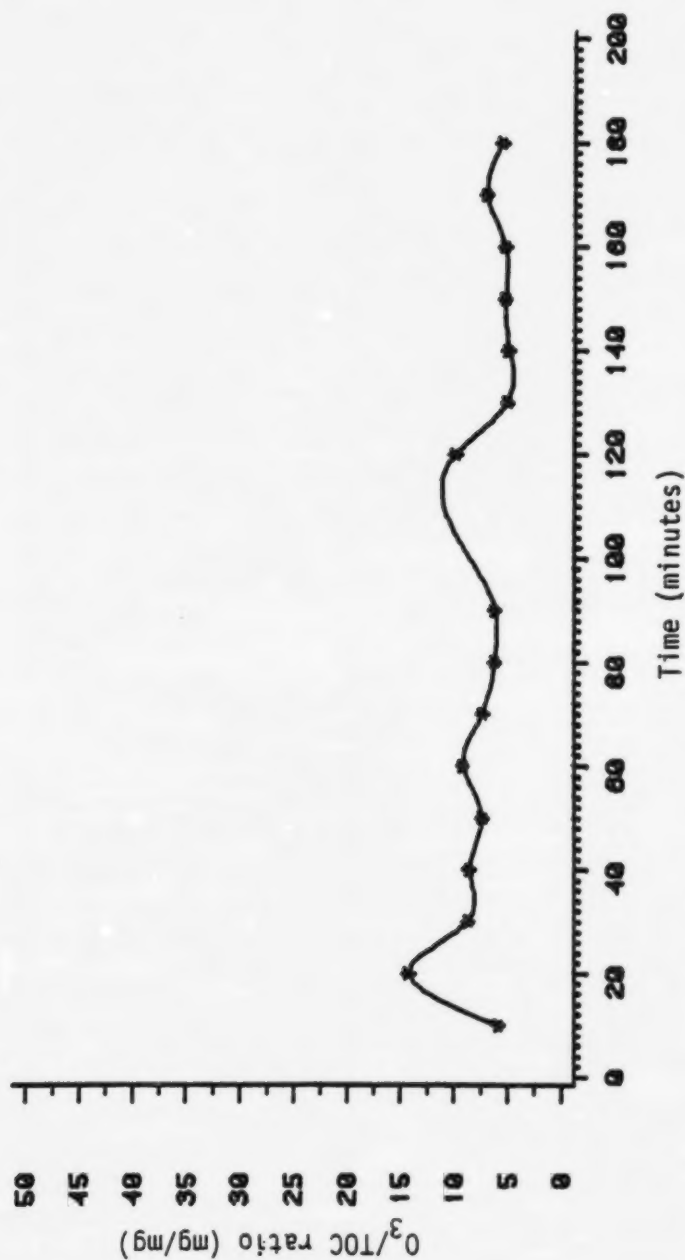


Figure C21. Time dependence of O₃/TOC ratio for sample B.

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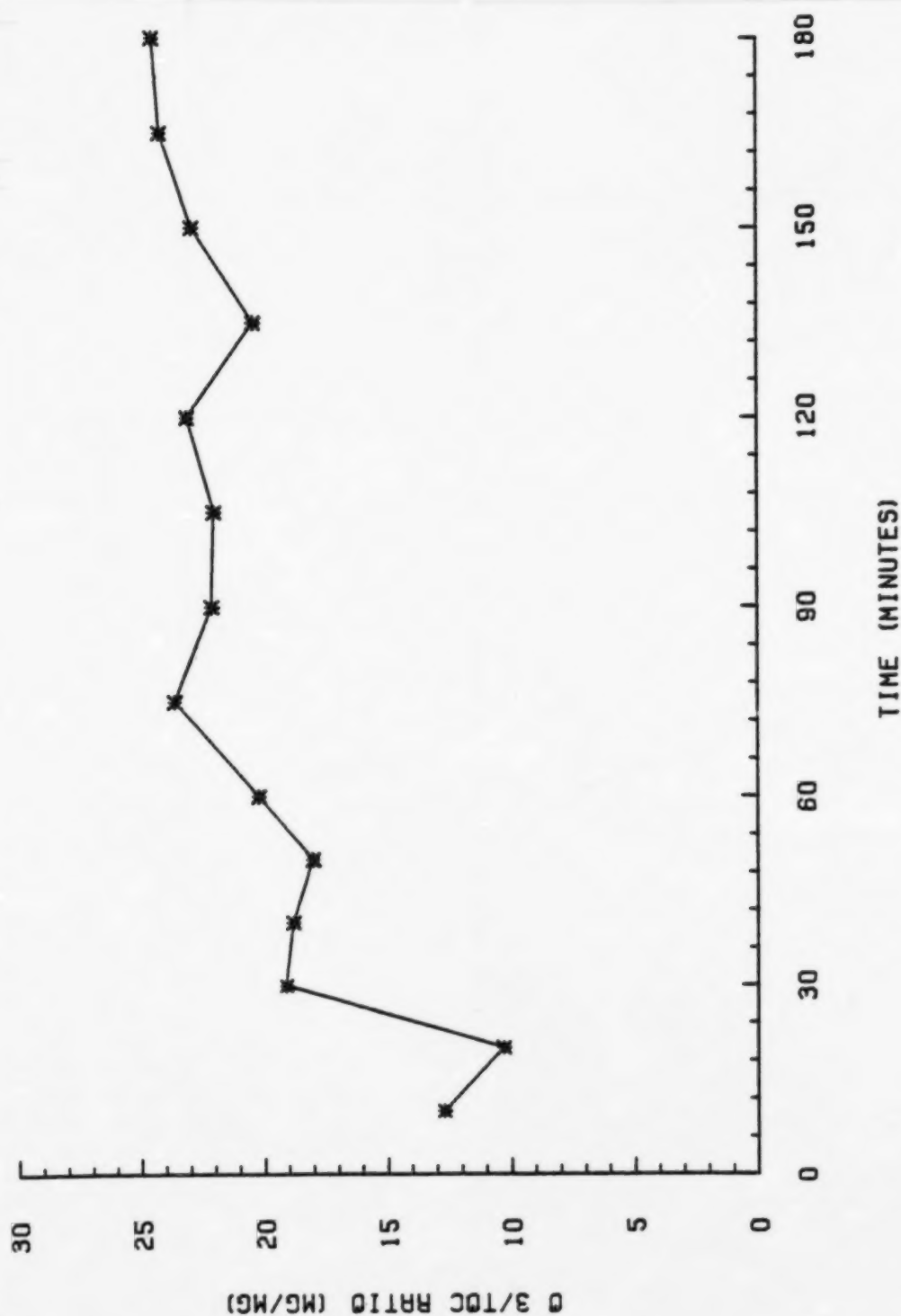


Figure C22. Time dependence of O_3/TOC ratio for sample C.

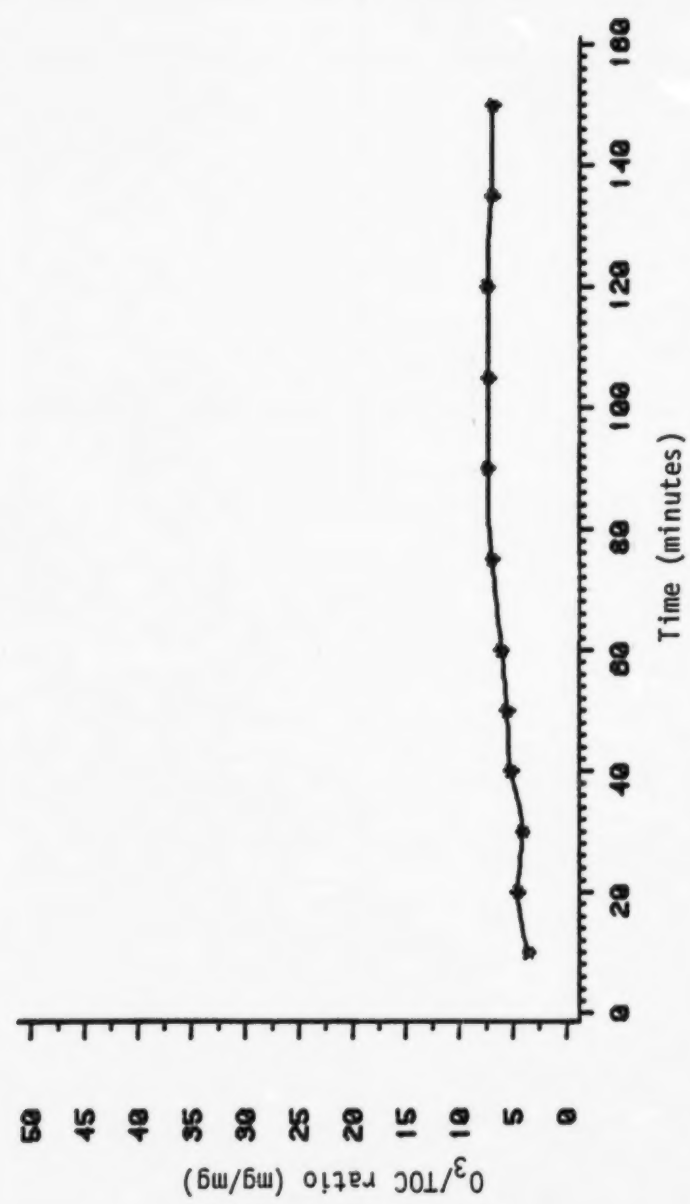


Figure C23. Time dependence of O₃/TOC ratio for sample D.

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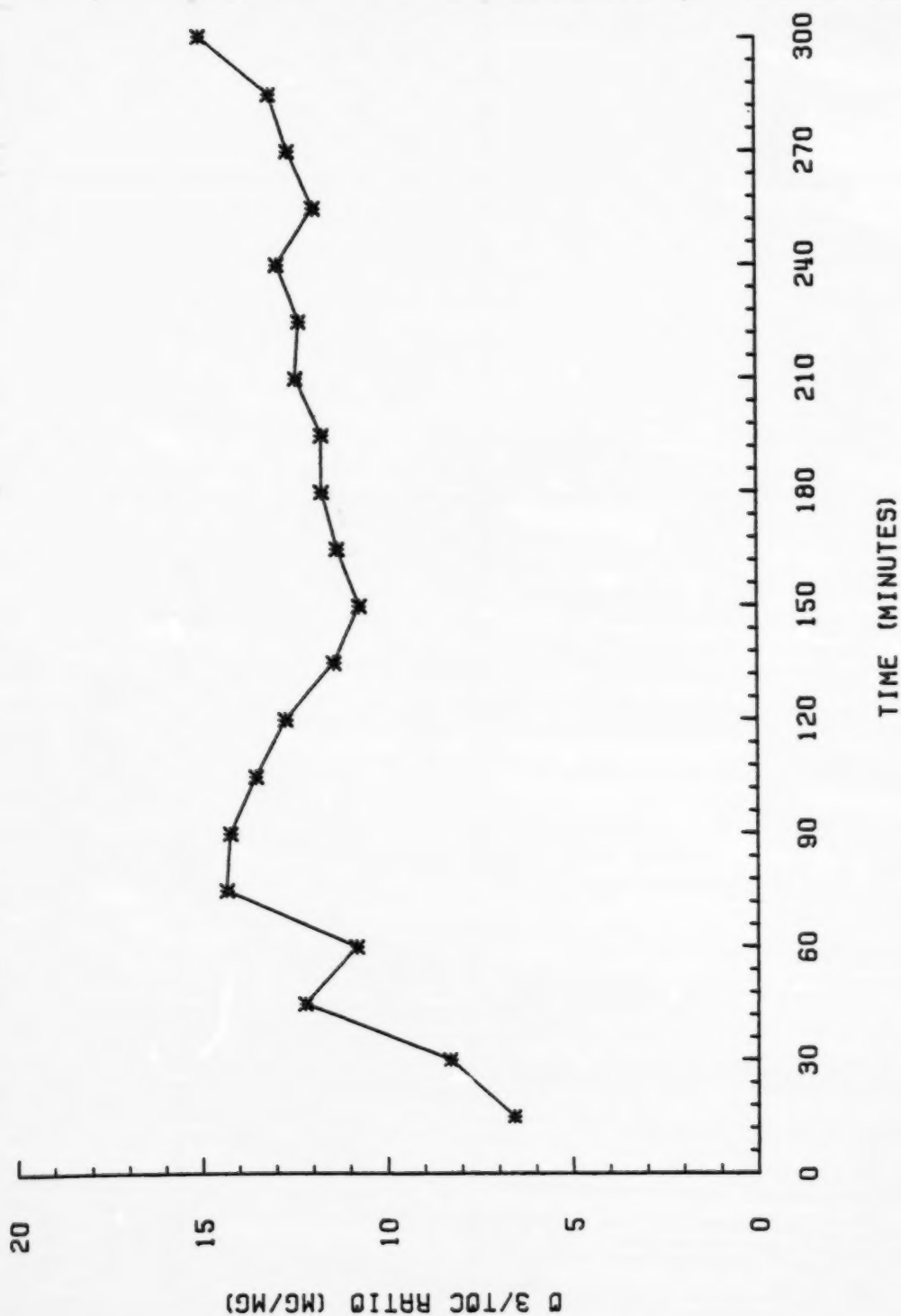


Figure C24. Time dependence of O_3/TOC ratio for sample E.

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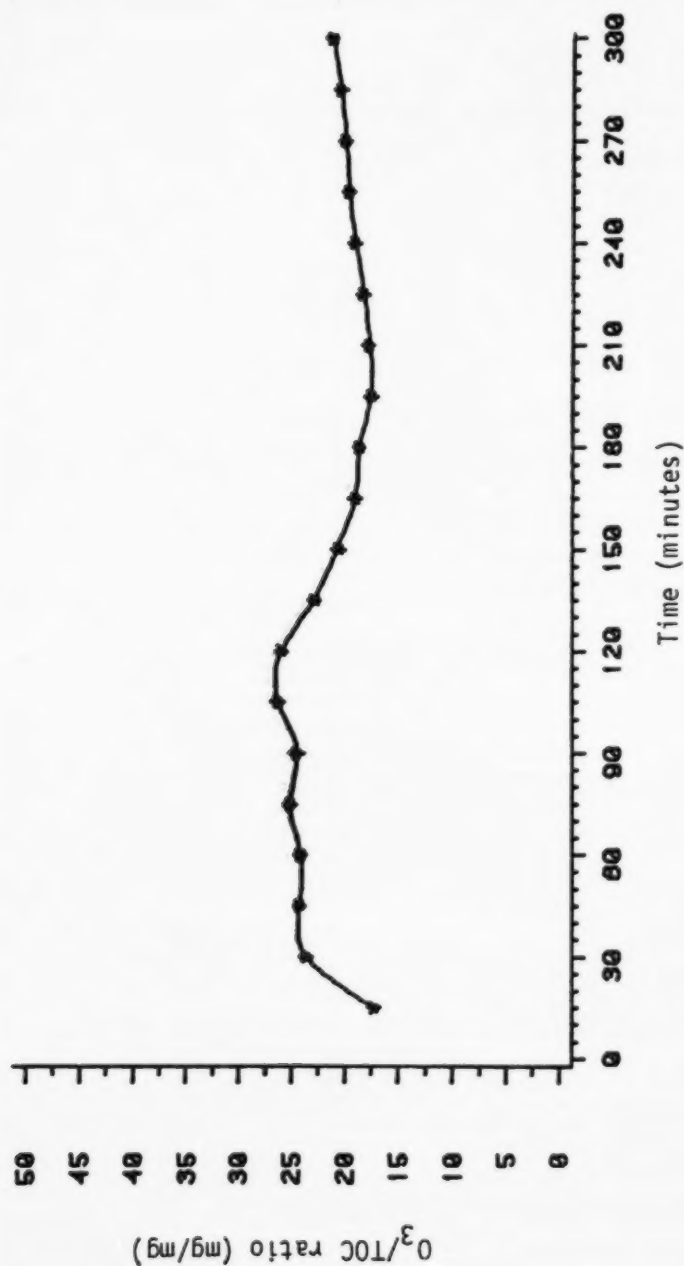


Figure C25. Time dependence of O₃/TOC ratio for sample F.

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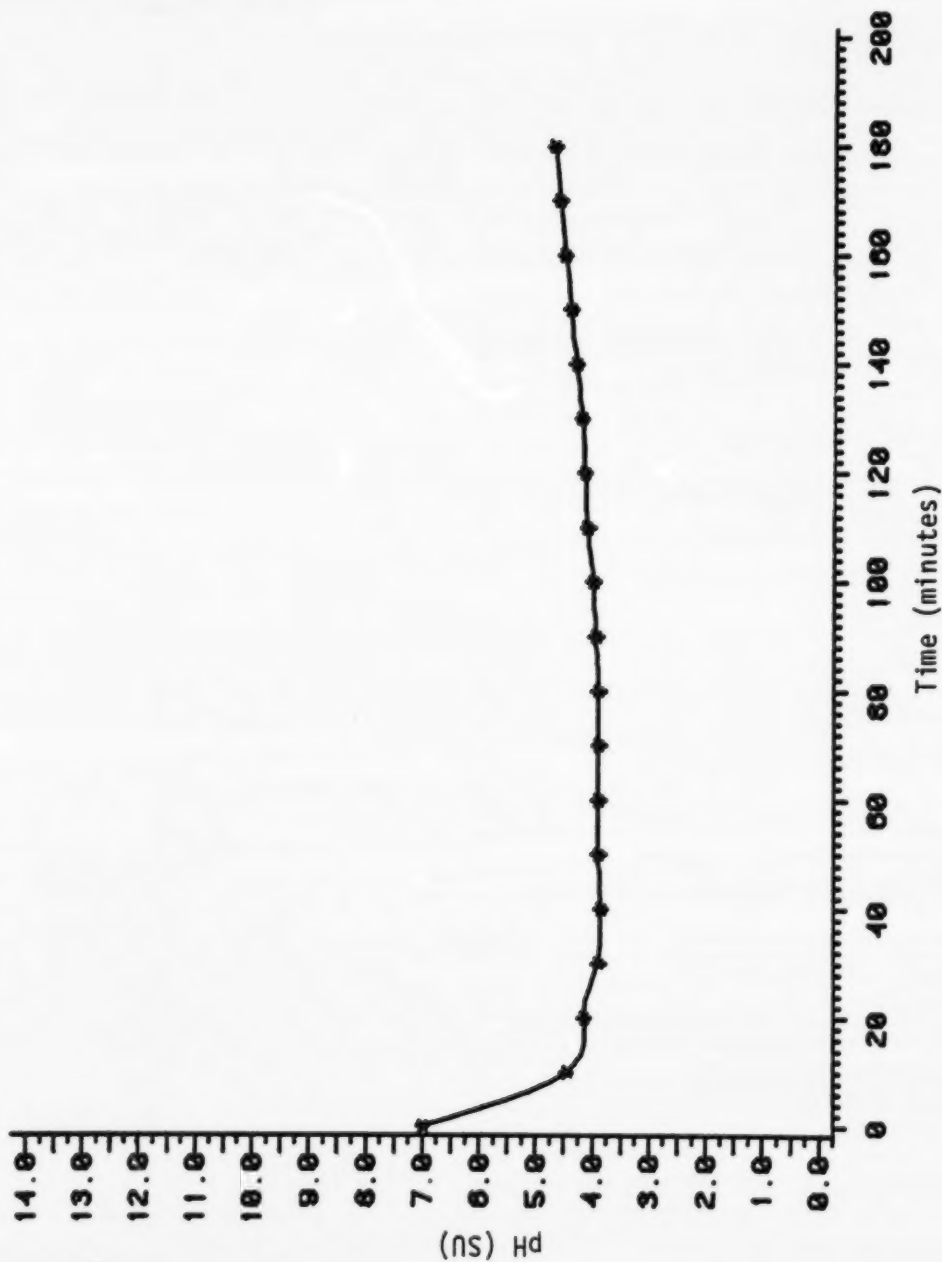


Figure C26. Time dependence of pH for ozonation of sample B.

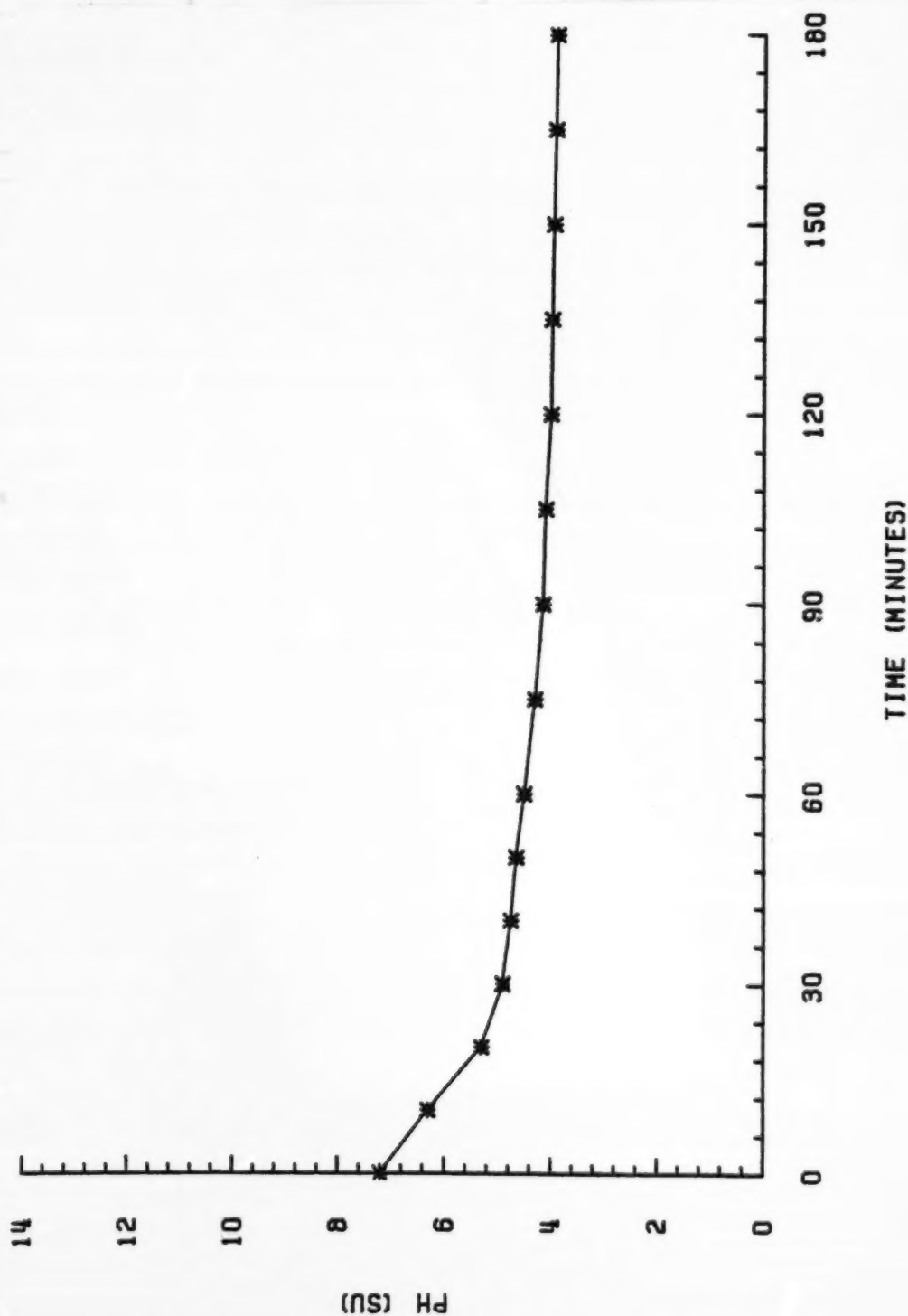


Figure C27. Time dependence of pH for ozonation sample C.

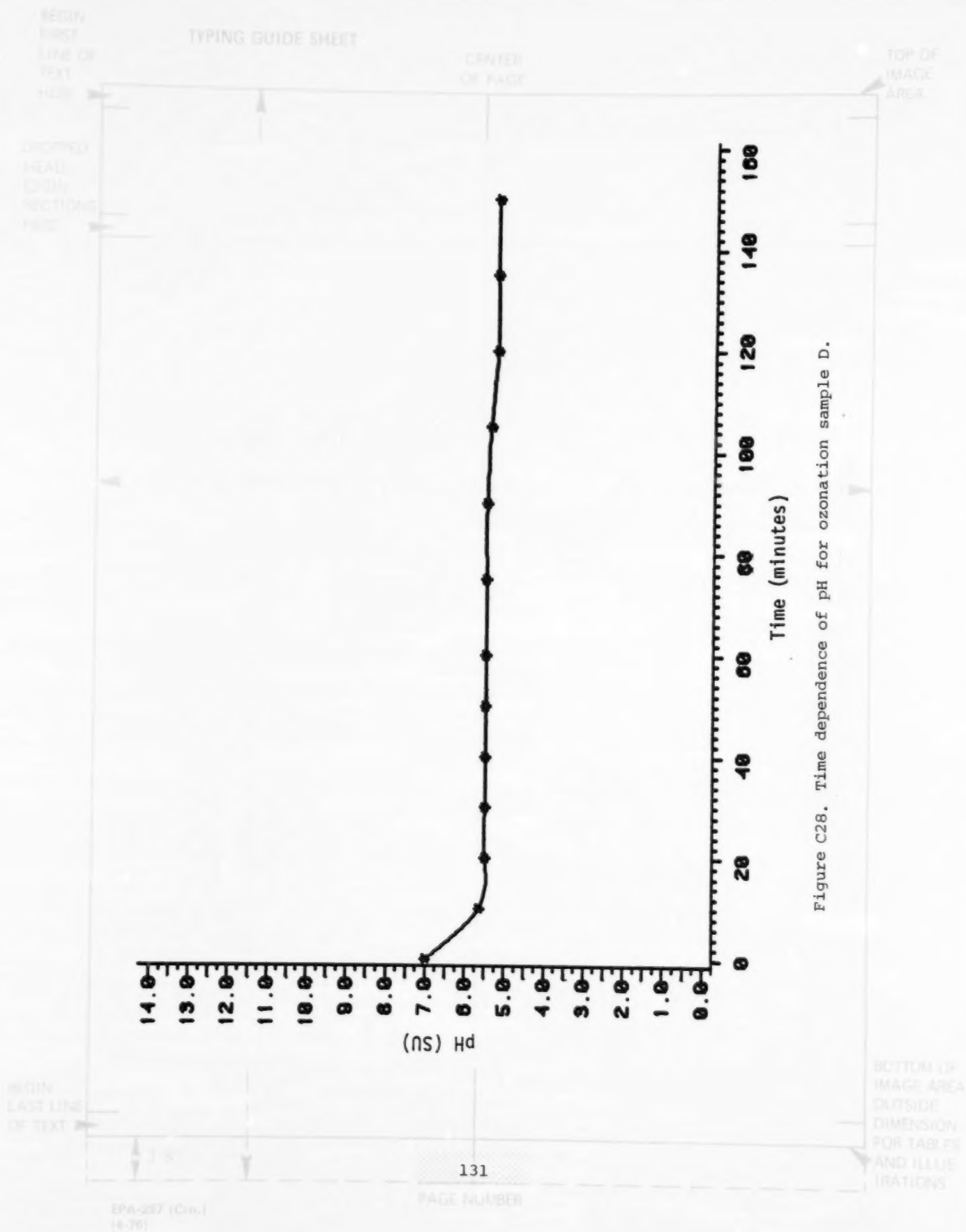


Figure C28. Time dependence of pH for ozonation sample D.

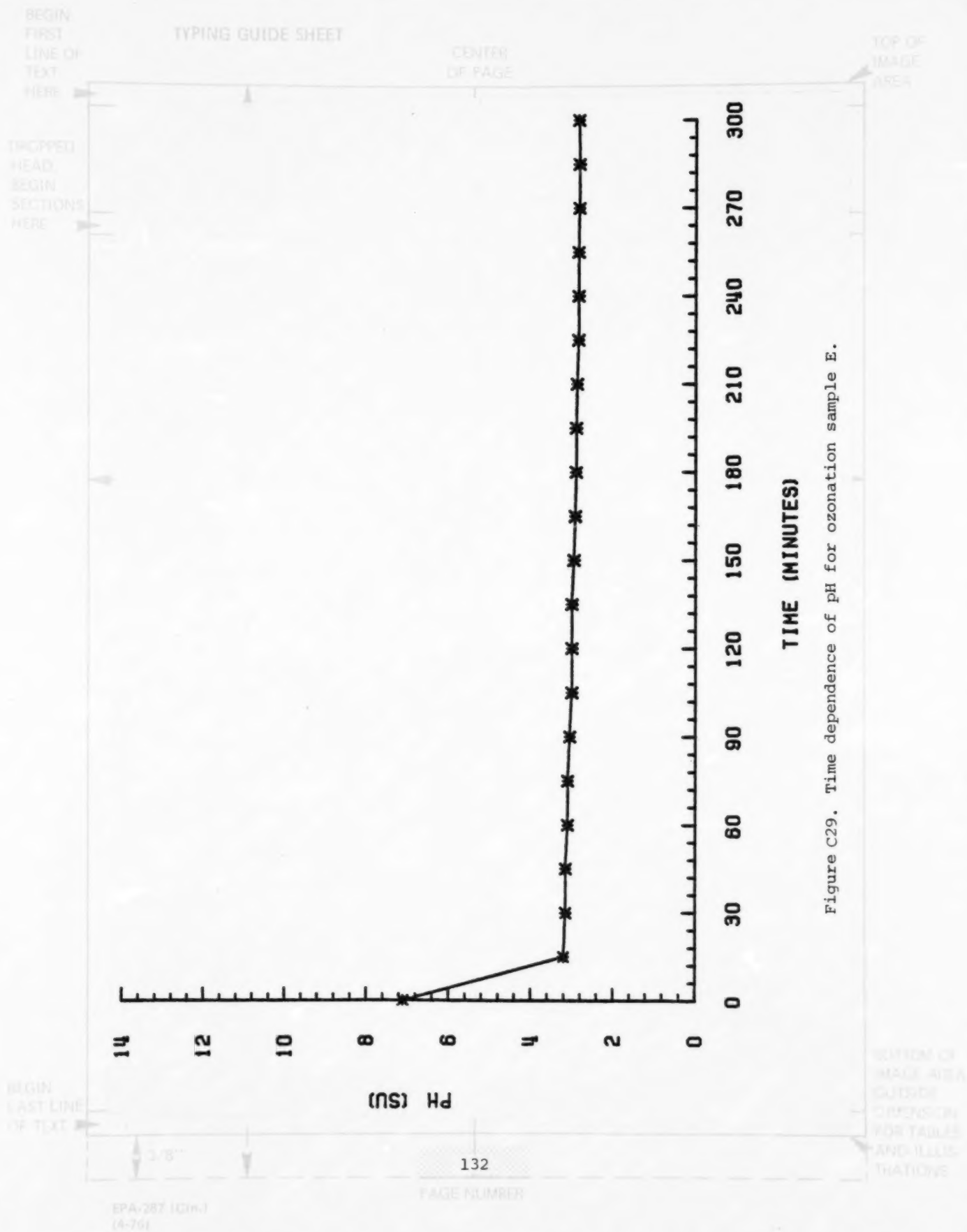


Figure C29. Time dependence of pH for ozonation sample E.

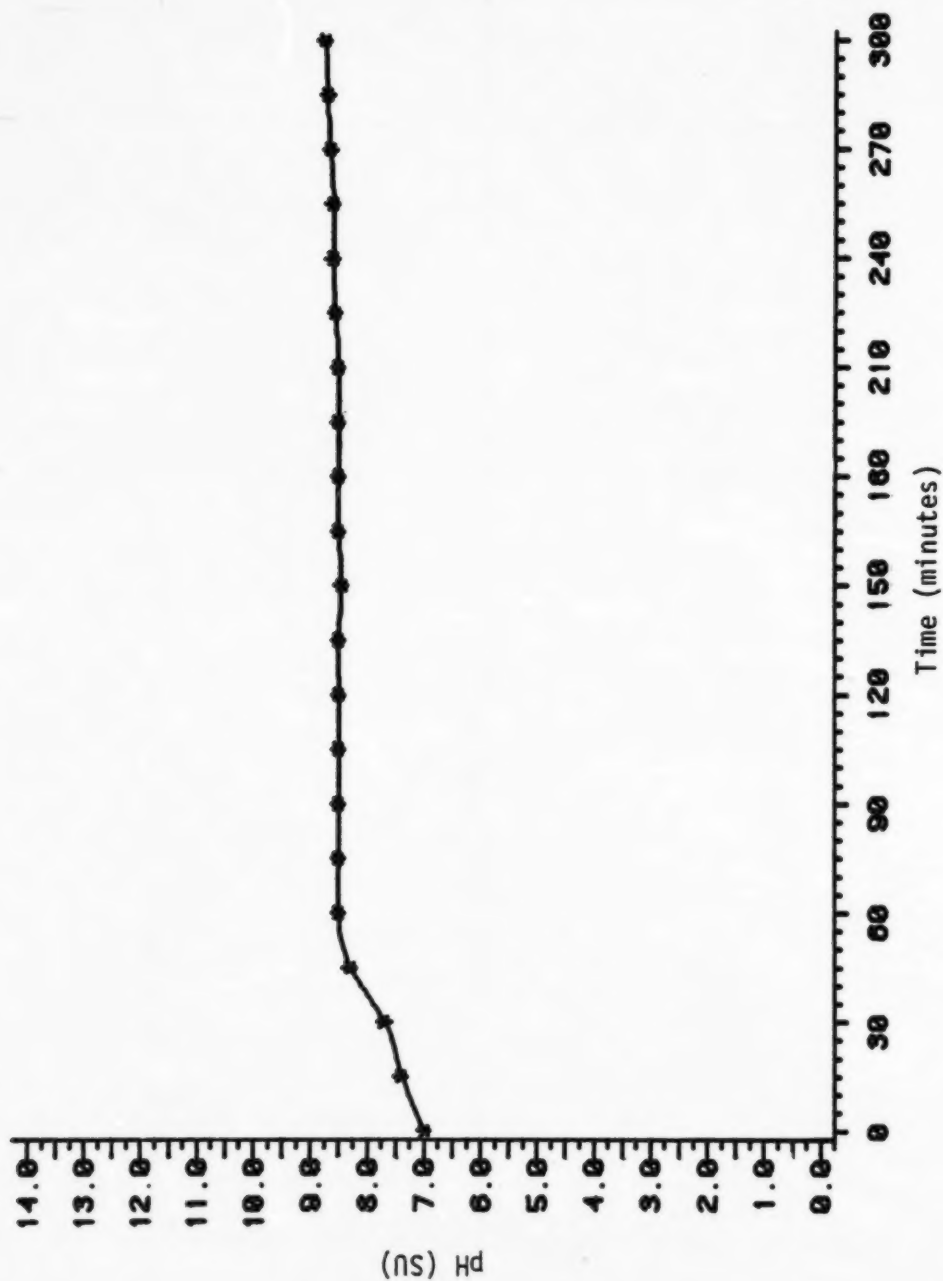
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Figure C30. Time dependence of pH for ozonation sample F.

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